

DEVELOPMENTS
SERIES

Developments in Reinforced Plastics – 2

**Edited by
G. PRITCHARD**

APPLIED SCIENCE PUBLISHERS



DEVELOPMENTS IN REINFORCED PLASTICS—2

Properties of Laminates

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PREFACE

This series will eventually cover the majority of the main topics of interest to those working with fibre-resin composites. Each volume consists of brief, readable reviews with a common theme; the theme in Volume 1 was the resin matrix. No attempt has been made, however, to achieve a balanced coverage of each theme, since this would involve duplicating excellent material already available. Instead, chapters have been chosen because of their practical importance, or because the topics have been left unreviewed for too long.

In considering importance, the editor has taken into account that the commercial viability of fibre-resin composites depends on several diverse factors — chemical, physical, engineering, economic and even aesthetic. Consequently, some of the properties discussed in this book are complex and not easily quantifiable. Nevertheless, they can be crucial in determining material selection.

It is hoped that this book will be read by newcomers to the composites field, as well as established workers. The first chapter is included mainly for the benefit of those unfamiliar with the problems of measuring the properties of laminates and similar materials.

The editor would like to acknowledge the cooperation of each author and the organisations they work for. Such people are invariably busy and are making their own personal contribution to the advance of composites technology. Their contribution to this second volume is much appreciated.

G. PRITCHARD

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Chapter 1

INTRODUCTION: CAUSES OF PROPERTY VARIABILITY

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SUMMARY

The physical and mechanical properties of fibre reinforced plastics have been intensively researched in recent years. It appears, however, that the values obtained are still subject to some uncertainty, and this is probably because they are so sensitive to precise material composition, specimen fabrication technique, sample conditioning procedure and test method. The details of these parameters are often omitted from published reports, whether on account of commercial secrecy, or simply for brevity. Sometimes it may be doubted whether the originators of publications have themselves obtained access to all the information necessary for interpreting property data. This introductory chapter discusses the factors affecting the properties of laminates, in general terms, and maintains that more progress could be made in the science of composite materials if more detailed disclosures of all relevant facts became accepted practice.

1.1 FIBRE-RESIN COMPOSITES

This chapter is intended chiefly for newcomers to the subject of fibre-resin composites. These composite materials are composed of a more or less brittle matrix reinforced with strong, stiff fibres. The matrix is

assumed to be an organic high polymer, and usually (but not necessarily) crosslinked.

Fibrous reinforcement can be incorporated into the matrix in the form of isolated filaments (continuous or discontinuous), or as filament bundles; as mat, or woven fabric of various kinds; as cloth, or as paper (as in decorative and electrical grade industrial laminates).

Materials described as laminates will be assumed to have a layered structure, in contradistinction to the non-layered structure of bulk moulding compounds (BMC; often called dough moulding compounds, DMC) and short fibre reinforced thermoplastics. The abbreviations GRP, CFRP and FRP refer to glass-, carbon fibre- and fibre-reinforced plastics, respectively.

1.2 DESCRIPTION OF COMPOSITE COMPOSITION

Leaving aside the fact that reinforced plastics compositions sometimes contain substantial quantities of substances other than matrix resin and fibre (particulate filler, powdered thermoplastic, elastomers and fire-retardant additives are notable examples) we can confine attention to the simpler two-phase composites. The briefest acquaintance with such materials demonstrates that the nature of these two phases does not suffice to determine the properties resulting from their combination. It is impossible to predict the mechanical, electrical, optical or thermal properties of a material simply from the fact that it is known to be, for example, a glass reinforced epoxy resin. Reasonable bounds can be set — there are limits to the tensile strength, stiffness, specific gravity, dielectric constant and thermal stability of a glass-epoxy or paper-phenolic laminate. But the full significance of information published in the literature giving numerical values for laminate properties requires the provision of considerable information about the composition of the material being studied, together with a description of fabrication procedure, sample history and conditioning, and the precise test method. Naturally this information is not always available, and it can be argued that the scientific literature is already voluminous enough. The question must be asked whether some of the literature reports of plastics and composites properties can have any real value without basic descriptions of the above matters.

This chapter considers some of the factors affecting composite properties. The first must be the composition of the composite; and this will be dealt with in the next section.

1.3 MAJOR VARIABLES

1.3.1 Resin

The terms 'epoxide',¹ 'polyester',² 'phenolic',³ 'polyimide',⁴ etc., are umbrella terms, each of which embraces a variety of polymeric substances⁵ (see Fig. 1.1). More precise descriptions are needed; ideally, we should know the reagents from which the resin was made, their proportions, the synthesis procedure and the results of a full chemical analysis of the product. This kind of information is routinely available to resin manufacturers carrying out their own testing programmes, but rarely to anyone else. A proper description of the matrix (which could contain a mixture of resins, and frequently does) should name the curing agent(s), their proportions and the cure schedule. However, a line has to be drawn somewhere, and most investigators either do not know, or know but cannot disclose, the more recondite details of their formulations. The important point is that these missing details may nevertheless be factors to consider when trying to account for apparent discrepancies between results obtained in different laboratories. Examples of parameters frequently omitted from literature reports are: the quantity of unreacted, extractable, non-bound matter in the resin;⁶ the molecular weight; the molecular weight distribution;⁷ the heat distortion temperature of the resin; the maleate-fumarate isomerization ratio in a polyester resin.

Reference to a code number can be a useful means of providing a specification, but this practice can be regarded only as a substitute for the explicit tabulation of resin characteristics. It may be the only possible description (as, no doubt, will be found in many instances in this book) but the investigators who resort to such shorthand specifications should ensure that their own knowledge is more comprehensive. Otherwise, the science of composite materials, and in particular of thermosetting resin-based composites, will be held back.

1.3.2 Reinforcement

Several reinforcing fibres besides glass and asbestos are now available — notably carbon or graphite, boron, aramid, aliphatic polyamide, etc. Glass can have a variety of different compositions denoted by letters (E, A, S, R, C) which indicate the quantity of sodium, boron, aluminium and other elements present. These differences are extremely important when considering the retention of composite properties after exposure to adverse conditions of climate or chemical environment. The great

majority of glass reinforcement used in the reinforced plastics industry is the E-glass type but the range of compositions met in research and development is of course wider than in the market-place. The physical form of the fibres is important; it may consist of monofilament, chopped strand, woven fabric or mat. The number of filaments per bundle influences both the mechanical and environmental properties. Filament length and diameter are also of interest. The surface density of reinforcing mats and fabrics is easily ascertained and should always be quoted. Finally, the volume or weight fraction of glass reinforcement should be given, as this is a major determinant of all mechanical properties.

Other fibres also come in several forms. Carbon is obtainable from several different precursor materials and is available in forms produced by heating the precursors to any of a wide range of temperatures. Asbestos is found with a number of distinct compositions, each with different properties. Fortunately, the same cannot be said of boron.

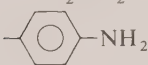
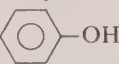
1.3.3 Interface

The boundary between resin and reinforcement is sometimes regarded as a third phase or 'interphase' region. Some kind of adhesive bond, whether physical, mechanical or chemical, is essential between matrix and fibres; this enables the matrix to transfer loads between fibres, thus improving toughness, stiffness, strength and creep resistance. It also enables the matrix to protect the fibres against mechanical damage or chemical attack. The interfacial bond requires close proximity between matrix and reinforcement.

Glass, and some other fibres, are surface treated to promote adhesion.^{8,9} Changes in surface treatment procedure can affect most of the mechanical properties of laminates, together with their environmental ageing behaviour and optical and electrical performance. Glass fibres have been traditionally treated with silanes, chrome complexes, cationic coupling agents and many other chemicals including mixtures of substances. Table 1.1 gives just a few examples taken from the very large number of silane coupling agents. The choice of coupling agent and its mode of application to the glass can have a definite influence on the mechanical properties of laminates.

The chemical used to improve fibre-resin adhesion is far from the only additive to glass surfaces. The size is also applied to filament surfaces for a number of reasons, one of which is to protect filaments from mutual abrasion during subsequent operations. Chopped strand mat contains an adhesive binder to keep the chopped fragments together — the choice of

TABLE 1.1
STRUCTURES OF SOME SILANE COUPLING AGENTS OF GENERAL FORM
 $X-Si-(Y)_3$

X	Y
$-CH_2CH_2CH_2NH_2$	$-OCH_2CH_3$
	$-OCH_3$
$-CH_2CH_2CHOCH_2CH(CH_2O)CH_2$	$-OCH_3$
$-CH_2CH_2CH_2OCH_2CH=CH_2$	$-OCH_3$
$-CH_2CH_2CH_2SH$	$-OCH_2CH_3$
$-CH_2CH_2CH_2OCOCH=CHCOOH$	$-OCH_2CH_3$
$-CH=CH_2$	$-Cl$
$-CH=CH_2$	$-OCOCH_3$
$-CH_2CH_2CH_2OC(=CH_2)CH_3$	$-OCH_3$
$-CH_2CH_2CH_2$ 	$-OCH_3$
$-CH_2CH_2CH_2OCOCH_3$	$-Cl$

binder, whether polyvinyl acetate, or bisphenol polyester-based, or some variant on these, can affect environmental stability.¹⁰ Other compounds used include lubricants and anti-static agents.

Carbon fibres require different procedures to improve fibre-resin adhesion. Usually this consists of an oxidation treatment,¹¹ and the kind of treatment employed can affect the interlaminar shear strength and other mechanical properties. The less graphitic forms of carbon fibre do not need surface treatment.

Given the nature of the interface condition, the resin and the reinforcement, together with the spatial distribution and orientation of the fibres, it ought to be possible to predict the likely numerical values of several laminate properties, if only on the basis of experience with similar compositions. The fact that experimental results do not always approximate to those expected can usually be attributed to one or more of three factors:

- (1) Fabrication technique.
- (2) Material history.
- (3) Variations in test methods.

These factors will be discussed briefly in the following sections.

1.4 FABRICATION

Table 1.2 lists some of the main fabrication methods for reinforced plastics.^{12,13}

TABLE 1.2
FABRICATION METHODS FOR REINFORCED PLASTICS

<i>Method</i>	<i>Typical resins</i>	<i>Typical end-product</i>
Hand lay-up	Polyester	Boat hulls
Spray-up	Polyester	Boats, chemical process equipment
Filament winding	Epoxy, polyester	Pipe, pressure vessels
Vacuum bag/autoclave	Epoxy	Aircraft components
Hot press moulding	Phenolic, aminoplasts	Electrical products
Cold press moulding	Polyester	Automotive products
Continuous lamination	Polyester	Roofing sheet, building panels
Pultrusion	Epoxy, polyester	Tubes, rods, channels
Injection moulding	Phenolic, polyamides, thermoplastics generally	Miscellaneous long-run mouldings

The method used invariably influences fibre orientation and distribution. It will probably affect the degree of cure of the resin — for example, large structures fabricated by hand lay-up in the open air will not be as nearly fully cured as hot-pressed laminates. The fabrication method also determines the nature and magnitude of internal stresses.¹⁴

One of the most important disadvantages of fibre-resin composites (shared by many other materials) is the fact that optimum theoretical properties are not attained because of the introduction of defects during fabrication.

1.5 CONDITIONING AND SAMPLE HISTORY

The initial properties of laminates, measured immediately after fabrication, can be subject to change. This could be very slight, and detectable only in the case of a few properties, or it could be substantial. The main

causes of property 'drift' include further resin cure, loss of trapped volatiles, absorption of moisture on storage and separation of a constituent phase. Perhaps the commonest of these causes is the absorption (or loss) of moisture (see Chapter 3). Composites generally contain a small quantity of moisture as a result of exposure to ambient laboratory conditions for some time. Opinions differ greatly about the best procedures for drying laminates. Complete removal of moisture by vacuum desiccation, with or without moderate heating, can be very slow indeed and in the case of thick sections can take months. On the other hand, strong heating of laminates containing substantial quantities of moisture — such as those which have been immersed in water — can produce internal cracks. Procedures for glass/epoxy materials vary from vacuum drying at ambient temperature for three or four months, to heating at 170°C for 24 h. Prolonged heating at a moderate temperature can anneal the matrix.¹⁵

The rapid drying of a laminate made from a brittle matrix can sometimes be seen to produce surface cracks. Figure 1.2 shows a glass/polyester laminate, exposed to hot water on one gel coat surface for a few weeks, 2 h after the water was removed. Exposure to ultraviolet light can also cause surface changes.

Finally, mechanical damage can be caused by rough handling and this is not always detectable to the naked eye.

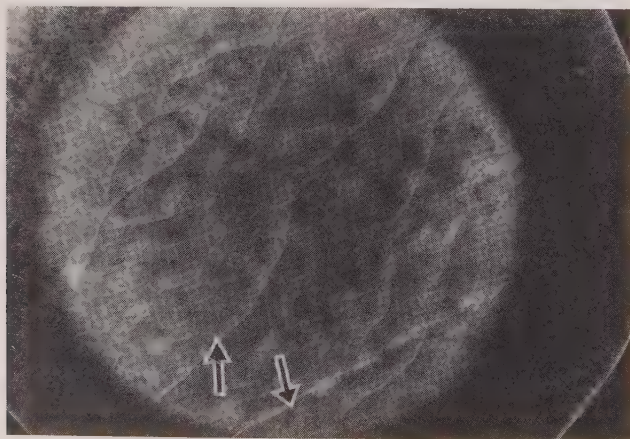


FIG. 1.2 Surface cracks in a polyester/glass laminate after drying. The laminate surface had been exposed to hot (80°C) water for a few weeks.

1.6 METHODS OF TESTING

So far, we have assumed that there are agreed methods for the determination of laminate properties, and that discrepancies between test results must originate in the materials themselves in some way. But there has not yet been time for the development of established and widely accepted test methods for composite materials. Procedures relating to important and widely used properties are still subject to controversy. The literature describes many methods for the assessment of the flammability of resins and composites; the measurement of impact strength is a matter for continuing discussion; the determination of laminate compressive strength and shear strength (see Chapter 5) still provides scope for further work. The applicability of linear elastic fracture mechanics and other fracture mechanics approaches to composites is still a controversial matter, and this affects practical methods for determining toughness.

This introduction cannot deal with specific questions, some of which in any case arise in subsequent chapters. The point to be stressed is that discrepancies in test data can often be traced to test procedures (this applies particularly to compressive strength) and so the details of test procedures are essential in reports of laminate properties.

Individual chapters carry reference lists which in many cases supply further information on individual test procedures.

1.7 CONCLUSIONS

To summarize, the properties of composite materials should be measured with knowledge of:

- (a) what the material constituents are;
- (b) how these constituents were combined into composite form;
- (c) how specimens were produced, and conditioned;
- (d) the critical factors in the selection of a test method.

A few examples from recent literature illustrate these points. Edge¹⁶ has described the significant effect on moisture absorption experiments, and related calculations, of a failure to dry specimens carefully before exposure. Illinger and Schneider¹⁷ report irreversible changes in an epoxy resin after a single wetting cycle; similar conclusions emerge from the work of Dewimille *et al.*¹⁸ Yamini and Young¹⁹ report large differences in epoxy fracture toughness parameters, simply as a result of

differences in hardener concentration. Roskott and Groenendaal²⁰ point out the connection between the selection of a polyester resin initiator system, the ultimate residual styrene content after cure and the physical properties of the cured resin. Hancox²¹ has shown the effect of specimen gauge length on the compressive properties of CFRP. Examples are commonplace and, in principle, known to everyone working in the field. The extent to which such factors can explain, confuse or invalidate results still needs emphasis.

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Chapter 2

IMPERFECTIONS IN FRP MATERIALS

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SUMMARY

Reinforced plastics, in common with all other structural materials, contain imperfections which detract from their physical and mechanical properties. These may be highly localised (e.g. cracks) or diffuse (e.g. an uncured matrix). They usually derive from the composite manufacturing process, but sometimes the subsequent history of the sample is responsible.

This chapter outlines briefly the main classes of defect, mentioning probable causes, appropriate means of detection and the expected implications for composite performance.

Much research still remains to be done in this field, particularly in relation to the elimination of voids and the assessment of their effect on properties, and also in connection with improved inspection techniques. Better control over fabrication procedures will produce great benefits for composite materials technology.

2.1 INTRODUCTION

No manufactured product is completely faultless. All practical materials contain imperfections, whether obvious or not. Sometimes these imperfections do not matter very much or their significance may be simply

cosmetic, but in some cases they give rise to noticeable changes in mechanical and other properties and occasionally they can lead to functional failure. A survey of defects in a wide range of composite materials including non-resinous matrix composites, has recently been produced¹ which reflects the widespread interest in and generality of this subject.

This chapter is intended as a brief summary of the main causes of laminate defects; of the methods used to detect defects, and of the importance of defects in detracting from optimum material performance. Being a summary, it cannot furnish detailed discussions of any one aspect such as a particular non-destructive technique, but more specialised reviews are already available, to which the interested reader can refer.^{2,3}

Reference will be made both to so-called 'advanced' high technology composites and to the more commonplace reinforced plastics materials and components, the designers and users of which could well look to aerospace technology for answers to some of their own difficulties.

Section 2.2 classifies the problems discussed in latter sections.

2.2 FAULTS

2.2.1 Faults in the Raw Materials

Raw materials are usually subjected to quality control and batch certification procedures which eliminate many of their more obvious possible shortcomings. The scope for problems is therefore reduced to factors such as:

- (1) Use of resin or pre-preg for which the proper storage temperatures have not been observed, or for which the shelf-life has expired.
- (2) Contamination of resin or additives after despatch to the fabricator.
- (3) Material variations caused by as yet insufficiently recognised inadequacies in the quality control and certification procedures.

2.2.2 Fabrication Faults

So many different kinds of fabrication faults are possible in theory that the subject might appear to defy classification, but in practice fabricators are concerned mainly with a limited range of common defects, namely:

- (1) Poor reinforcement impregnation with or without the production of resin-rich regions.

- (2) Gel coat imperfections such as pin-holes, wrinkles, cracking and poor adhesion of gel coat to laminate backing.
- (3) Faulty joints (see Section 2.2.3).
- (4) Resin undercure (see Section 2.4).
- (5) Incorrect fibre volume fraction (see Section 2.6).
- (6) High void content (see Section 2.8).

Other problems peculiar to the use of stacked plies of pre-preg include:

- (7) Fibre mis-alignment.
- (8) Inter-ply delamination (see Sections 2.7 and 2.9.1).
- (9) Translaminar cracks.

Specific problems are sometimes related to the manufacture of actual components rather than the production of the composite material *per se*. For example, Marshall and Rhodes⁴ have examined the importance of shape imperfections in the production of GRP shell structures. The separation of pipe linings from the walls is another illustration.

2.2.3 Jointing and Fastening Faults

Measurements of the properties of simple FRP coupons do not take into account the strength of joints, which could be intrinsically weak or marred by defects. The reinforcement plies themselves must be combined in such a way as to avoid weak overlaps or butt ends. The individual components need to be fastened soundly together to form a structure; and the whole structure may have to be attached firmly to something else.

Joints should not be significantly weaker than the material itself, and should not lead to the application of loads of a kind the material is least able to withstand. For example, unidirectional CFRP has poor shear strength in the direction parallel to the fibres and unfortunately metal fastenings can readily subject CFRP to shear rather than tensile stresses. To overcome this, adhesive bonding methods have been developed. Green and Phillips⁵ report a crimp-and-bond technique, enabling aligned fibre composites to retain high mechanical strength during axial loading.

Shelton⁶ has listed a large number of possible defects in adhesively bonded sheets. Stone² offers a shorter list, mentioning:

- (1) Faults in the adherend geometry.
- (2) Surface preparation faults.
- (3) Incorrect adhesive geometry.

- (4) Improper selection or use of adhesive.
- (5) Weak interfaces caused by the presence of (for instance) mould release agents.

Galvanic corrosion with metal-to-CFRP joints is a design problem which surfaces only after the component has experienced exposure to moist conditions for some time. The drilling of CFRP for subsequent insertion of metal bolts or bushings, for instance, exposes fibre ends devoid of any resin coating and facilitates the setting up of a galvanic cell, thus corroding the bolt. Titanium is only slightly affected, aluminium rather more seriously and cadmium-plated steel very extensively.⁷ But the rate of corrosion can be drastically reduced by electrical isolation with suitable coatings.⁸

2.2.4 Defects Arising During Service

The problems considered under this heading and discussed more fully in subsequent sections are those originating in some post-fabrication experience, such as:

- (1) Mechanically induced defects arising from impact, static overload or fatigue.
- (2) Defects arising from contact with hostile environments, chiefly aqueous fluids.

Fatigue is discussed fully in Chapter 4. It cannot be entirely divorced from the fabrication faults listed in Section 2.2.2 because the initiation of fatigue damage can be related to fabrication.

Most of the above-mentioned defects can affect the properties and functional usefulness of FRP. They are not always visible to the naked eye, and so specific detection techniques have been developed. These will be summarised in the following section.

2.3 INSPECTION TECHNIQUES

2.3.1 Ultrasonic Methods

Ultrasonic methods of inspecting composites are non-destructive, whereas some of the alternatives affect the materials under test in obvious or subtle ways. Figure 2.1 depicts the principle of the method. A laminate AB is placed between a transmitter C and a receiver D. The sample may be immersed in a water bath, to achieve constant coupling between probes. The

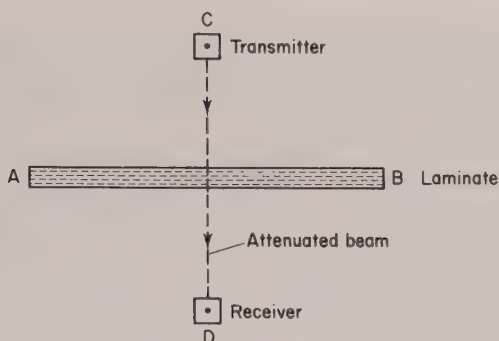


FIG. 2.1 Principle of ultrasonic inspection technique.

attenuation of the beam can be measured directly or, if the receiver is dispensed with, after reflecting from the back wall of AB and returning to a transmitter-receiver at C. The attenuation is recorded and displayed in the form of a quantised C-Scan, the darkest regions having the lowest attenuation.

Figure 2.2 shows a voided region in a carbon-epoxy laminate.

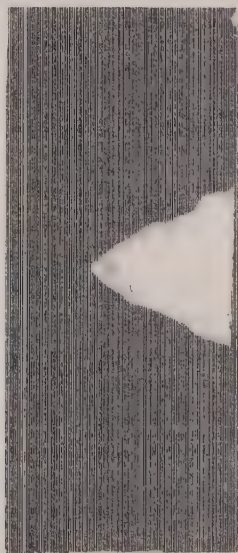


FIG. 2.2 Ultrasonic C-scan of a carbon-epoxy laminate. Dark regions show lowest attenuation.

Attenuation depends on laminate thickness, void content, surface quality, fibre content and number and size of delaminations. The method is particularly useful for measuring void content (see Section 2.8.2) and for locating regions where the porosity within a given laminate is high. It is also useful for detecting delaminations in multi-ply lay-ups. At the same time, the velocity of the pulse can be measured.

Ultrasonic waves can be used to simulate the acoustic emissions caused by mechanical damage and therefore enable acoustic emission (Section 2.3.5) to be deployed without damaging the material.

2.3.2 Radiography

Gamma rays and soft X-rays are absorbed by glass much more than they are by unfilled, unpigmented resin. A whole laminate, or a whole adhesive bondline, can be examined to show inclusions and fine cracks. The resolution obtained is poor, unless a very fine microfocus is used to survey a much more limited area. Radiography can be used to check fibre alignment, fibre buckling, lay-up direction and lay-up order, using pre-preg sheets doped with dense lead glass fibres.⁹

Figure 2.3 shows a high-definition X-radiograph of a triaxial carbon fibre composite showing resin-rich zones (dark in colour), fibre mis-orientation and chemical contamination.

2.3.3 Penetrant Methods

Fluorescent dye and radio-opaque penetrants such as di-iodomethane can be used to highlight fine cracks, particularly surface cracks and also to detect pin-holes. Some penetrants could produce alterations in the material.

2.3.4 Thermography

This technique locates flaws because they produce non-uniform heat transfer, and hence temperature discontinuities. The temperature discontinuities are translated into colour changes by means of various indicating devices; one of the simplest indicators is the cholesteric liquid crystal, applied as a slurry or on film or paper.¹⁰ Infrared thermography utilises an infrared camera as indicator, and can be applied to the detection of surface cracks, delaminations and blind-surface impact damage, by means of an arrangement such as that depicted in Fig. 2.4. McLaughlin *et al.*¹¹ found that patterns could be obtained from frictional heat generated by CFRP subject to small cyclic stresses (5% of ultimate

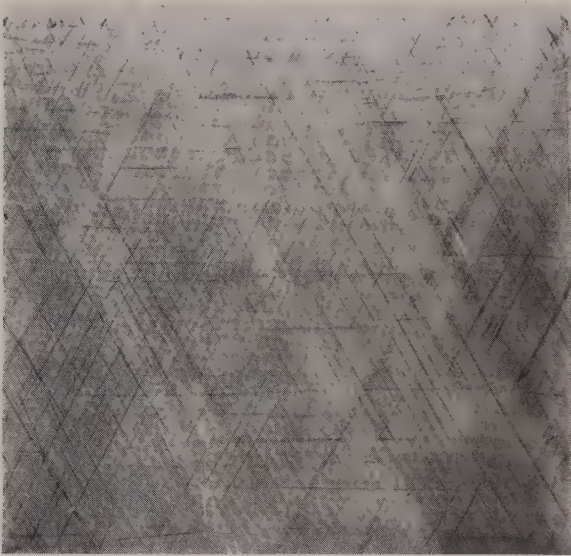


FIG. 2.3 High definition X-radiograph of a triaxial carbon fibre composite, showing resin-rich zones, fibre misalignment and chemical contamination. (Courtesy of the Non-destructive Testing Centre, Harwell, UK.)

fracture stress at 1 Hz) provided the specimens contained cracks with sliding surfaces. Holes and notches were not detected.

2.3.5 Acoustic Emission

This subject has been extensively reviewed elsewhere, so only a brief description is required here.

Acoustic emission utilises the principle that stress waves are generated when stored strain energy is released, with small local failures taking place. The normal method of application is to attach transducers (such as piezo-electric crystals) to a sample, and amplify the signal produced by an applied load. Emissions below a certain arbitrary amplitude are ignored and the total number of higher amplitude emissions is recorded as a function of applied load or time. Acoustic emission, employed in this way, is not a non-destructive test, although procedures can be devised which are to all practical purposes non-destructive.

The technique can indicate the stress required to induce serious irreversible damage. Interpretation of the data is still a matter for debate,

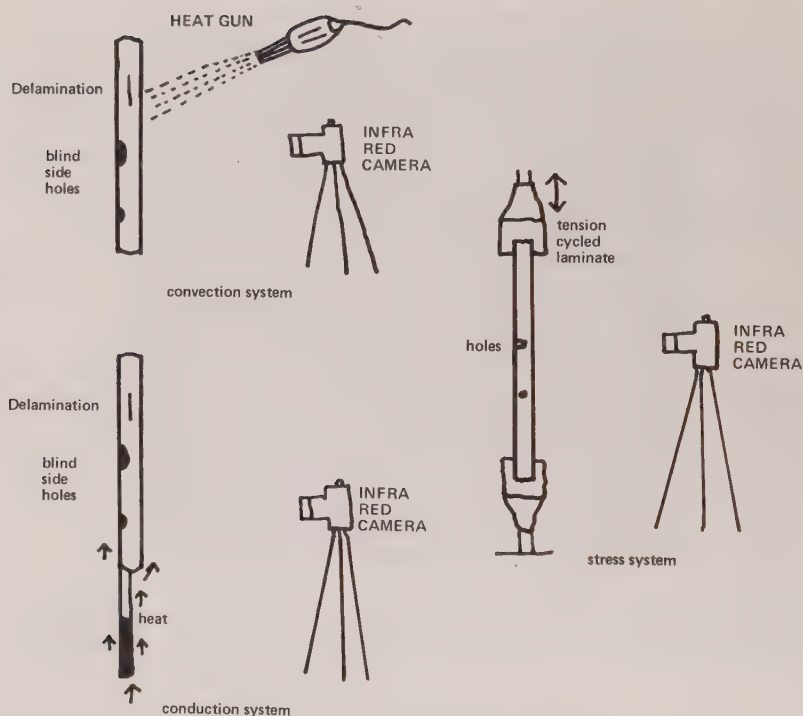


FIG. 2.4 Principle of infrared thermography.

but commercial equipment is widely used for monitoring FRP structures. Such an assembly is shown in Fig. 2.5; this is a 32-channel field testing system. Figure 2.6 is a developed view of a reactor vessel, showing the location of acoustic emission sources (S1, S2 etc.) These sources could be located by triangulation.

The laboratory use of acoustic emission techniques to study the onset of damage and failure in composites is still being developed.¹²⁻¹⁴ Initial emission at very low tensile strain rates is believed to be caused by fibre-resin debonding and resin microcracking, typically at 0.1 to 0.5% elongation. Above a certain stress threshold, emission continues when the load is held constant, because of stress redistribution caused by matrix flow. Removal and gradual restoration of the load causes emission at a lower stress level than that previously reached; the ratio

$$\frac{\text{new load required for emission}}{\text{previous maximum load}}$$

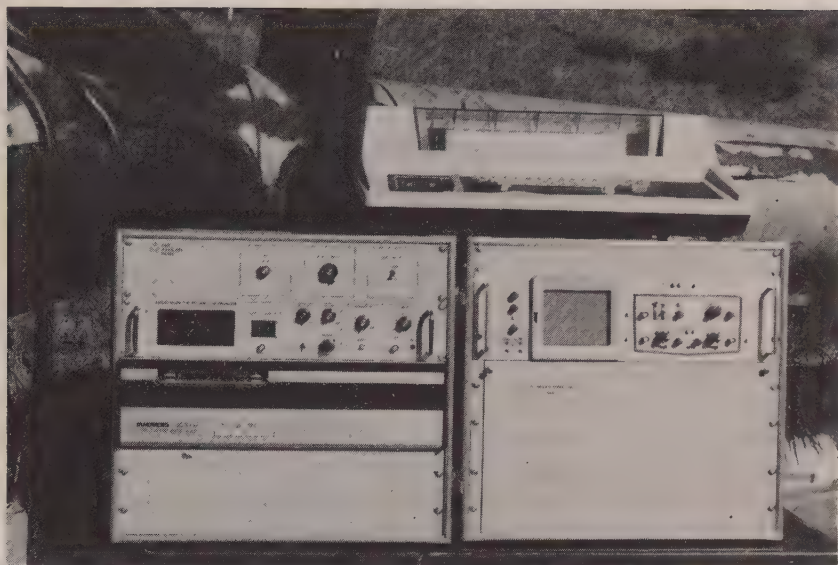


FIG. 2.5 32-Channel acoustic emission field testing system (courtesy of Endevco, Royston, Herts, UK.)

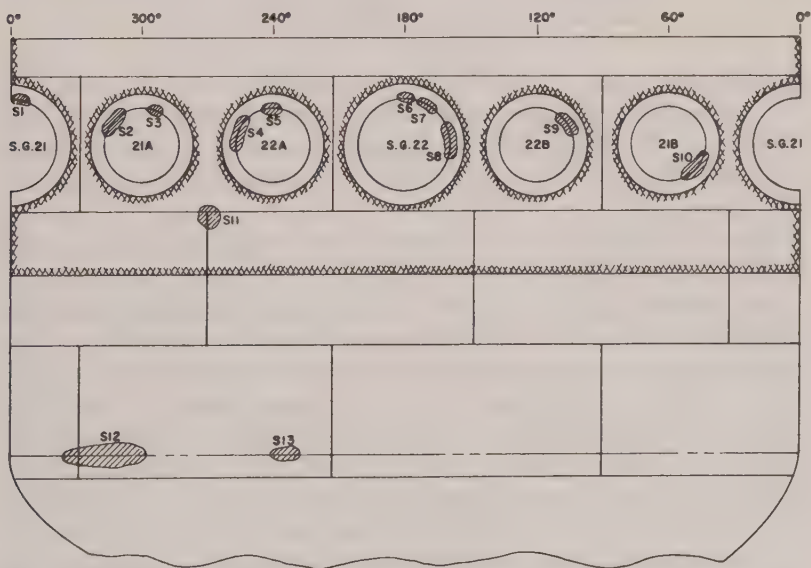


FIG. 2.6 Reactor vessel showing the location of active sources of acoustic emission. (Courtesy of Endevco, Royston, Herts, UK.)

is known as the Felicity ratio, and can be correlated with the damage induced. (The Felicity effect is employed in testing in-service vessels.) Prior to failure fibre fracture produces high amplitude emissions.

In theory, whole components can be checked without their being taken out of service, whereas other techniques either require removal from operation or provide information on a very limited zone. In practice, the generation of spurious signals is a problem, and it may be necessary for a test to be carried out near to the design stress of the article under test. According to Phillips and Harris¹⁵ the precise structure of the laminate or component has a major effect on its emission characteristics.

2.3.6 Other Methods

The search for rapid, simple, non-contacting and unambiguous techniques for detecting defects continues. Among existing NDI methods, mention should be made of *holography*¹⁶ which can detect debonds between a CFRP skin and a honeycomb core, or between other bonded surfaces; of *eddy-currents*,¹⁷ used for determination of lay-up order in crossplied CFRP, and of *neutron radiography*,¹⁸ again used for bond-like defect detection.

2.4 RESIN UNDERCURE

An undercured resin matrix is not a localised defect such as a hole or crack, but it is certainly an imperfection, despite being dispersed throughout the material. Moreover, it is sufficiently important to have received widespread attention from quality control specialists and others for several years.¹⁹⁻²¹

Definition of completeness of cure is a controversial question, but from the chemical standpoint, completion is reached when all potentially reactive chemical groups have been constructively used in the creation of a covalently bonded network. In practice, this point is seldom strictly attained, because of diffusion control, but it is possible to approach the maximum degree of reaction. Postcure at progressively increasing temperatures overcomes diffusion control, and enables polyester cure reactions to proceed to as much as 99.5% of the theoretical extent. This results in the optimisation of most of the resin and composite properties (see Fig. 2.7), although prolonged postcure can adversely affect specific properties, such as impact strength, and an overall balance has to be sought.

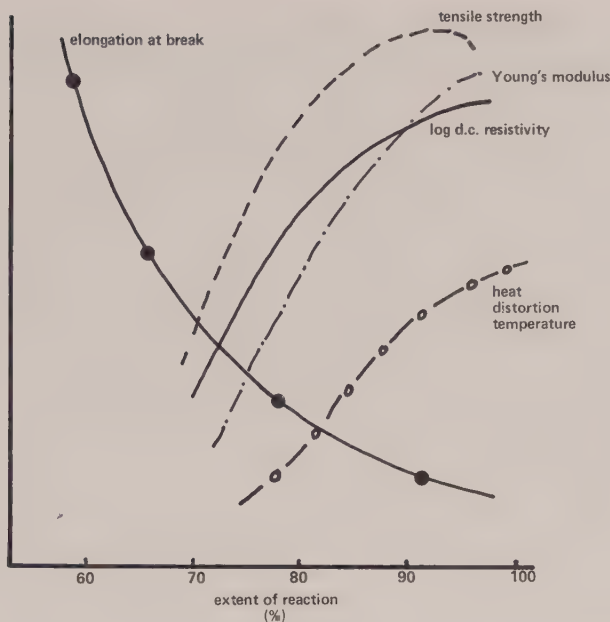


FIG. 2.7 Influence of extent of curing reaction on the properties of an unreinforced polyester resin (vertical axis: qualitative only).

Achieving maximum cure requires the correct resin-to-hardener ratio, a suitable temperature-time programme²² and the absence of cure inhibitors (for example, sulphur inhibits the cure of unsaturated polyester resins).

Determination of the degree of cure of a resin has been attempted by many methods, chiefly by monitoring (i) mechanical property changes, e.g. Barcol hardness, dynamic shear storage modulus and loss factor, tensile and flexural properties, and ultrasonic attenuation, (ii) electrical parameters, such as dielectric constant and loss, and d.c. volume resistivity, (iii) measuring various physical properties, e.g. specific gravity, refractive index, extent of solvent uptake, and quantity of extractable matter, and (iv) estimating the extent of the chemical reaction, by wet analysis, by spectroscopic or gas-chromatographic techniques, or by thermal analysis.

Methods suitable for laboratory specimens under carefully controlled conditions are not necessarily suitable for real components. Some are clearly not intended for practical use, but only for studying factors likely

to affect cure performance. Phillips and Bader²³ investigated the differential scanning calorimetry technique. They found it less useful than measurement of strain energy release rate (using double torsion geometry), but this method discriminated between cure states only at 80°C or above. The use of high temperatures is in itself capable of changing the degree of cure, especially if the test temperature exceeds the cure temperature. Certainly an undercured composite is likely to display anomalous and inferior mechanical properties at high temperatures (since the matrix will be approaching its pseudo-rubbery state), but this approach is less useful in practice than those methods lending themselves to continuous, in-mould monitoring, such as d.c. resistivity²⁰ and ultrasonic attenuation measurement.²¹ These methods ought to be capable of detecting gross undercure through failure to dispense adequate quantities of hardener, for example.

Another problem is the determination of degree of cure of thick samples, whether of cast resin, filled resin or laminate. Thermal gradients occur during the cure of thick sections, caused by the varying distance from the press platens, by the exothermic heat of reaction and by the positioning of metal heat sinks such as inserts. In other words, the degree of cure may be far from uniform throughout the component. The best available methods, such as dielectrometry and ion graphing, simply record the average value of a specific property.²⁴

2.5 MOULDED-IN STRESSES

Residual stresses remaining in laminates after fabrication can result in warping. Curtis²⁵ has investigated the curvatures of some CFRP and GRP laminates of asymmetrical (0°, 90°) construction. The GRP systems showed smaller tensile strains perpendicular to the fibres, but larger compressive strains parallel to them. This was explained by the greater anisotropy of the CFRP materials, which resulted in residual tensile strains equal to a significant fraction of the strain at failure. Absorption of moisture reduced these residual moulding strains to zero at saturation, but since in practice moisture saturation is rarely achieved, exposure to humid environments could provide only a partial and reversible relief of strain. The warping described does not occur in balanced laminates.

The linear thermal expansion coefficient of reinforcing fibres is typically less than 10 per cent of that of the matrix resin. Therefore, the resin constrained by neighbouring fibres is unable to shrink on cooling. The

coefficient of expansion of a composite layer is much greater in the transverse than in the 0° direction. The existence of neighbouring plies of differing orientations ensures the development of residual stresses in each layer.

The necessary information for calculating these thermal effects is still being collected. Kabelka²⁶ has described a mathematical model for calculating thermal expansion coefficients and thermal stresses in composites.

Transverse cracks form when the tensile stresses normal to the fibres become large enough. The mechanisms of initiation and growth of these cracks have been investigated by Aveston *et al.*,²⁷ Wang,²⁸ Bailey *et al.*²⁹ and by others. Thick laminae probably contain more defects, and fail at lower stresses, than thin ones; they also contain more strain energy for surface creation. Wang used the elastic energy release rate approach to analyse the onset and development of transverse cracking and edge delamination.

2.6 FIBRE VOLUME FRACTION

Standard methods have long been available for the determination of glass content, in absence of other inorganic or non-volatile matter, by destructive ashing at 575–600°C. Acid digestion methods have also been developed for the destructive measurement of carbon fibre volume fraction. The non-destructive examination of actual components to check glass content is much more difficult, but three approaches have been described.³⁰

Ultrasonic pulse propagation methods have been tried to assess whether a ply of glass has been omitted inadvertently from a laminate. The simplest approach assumes a known relationship between wall thickness and the number of plies, and the ultrasonic tool just measures thickness. The velocity of the ultrasonic wave in resin has to be known; fortunately, there is not a great variation between different polyester resins, although, as already indicated earlier, the velocity does have some dependence on the degree of cure.

GRP has a high damping capacity for ultrasonic waves and it also suffers from scattering of the waves by the reinforcement—this obscures any back-echo. Broad-frequency band pressure wave transducers overcome these problems to some extent.

The above procedure assumes no access to one side of the laminate. In

cases where both sides are accessible, X-radiography has been attempted, but it is restricted to unfilled resin systems, and has several disadvantages.

A measure of glass content has been attempted by relating it to the dielectric constant of the laminate at microwave frequencies. This too is dependent on the absence of filler, pigment, air bubbles, etc. Nevertheless, with this qualification good correlations have been reported with direct ashing results.³⁰

2.7 DELAMINATION

Edge delamination (mentioned also, briefly, in Sections 2.5 and 2.9.1) can arise from the high out-of-plane normal or shearing stresses produced in the vicinity of edges, and has been shown to occur when carbon-epoxy samples containing circular holes are compressed. Figure 2.8 shows the effect of 25.4 mm holes on the compressive strength of carbon-epoxy laminates, loaded in such a way that buckling was suppressed. The

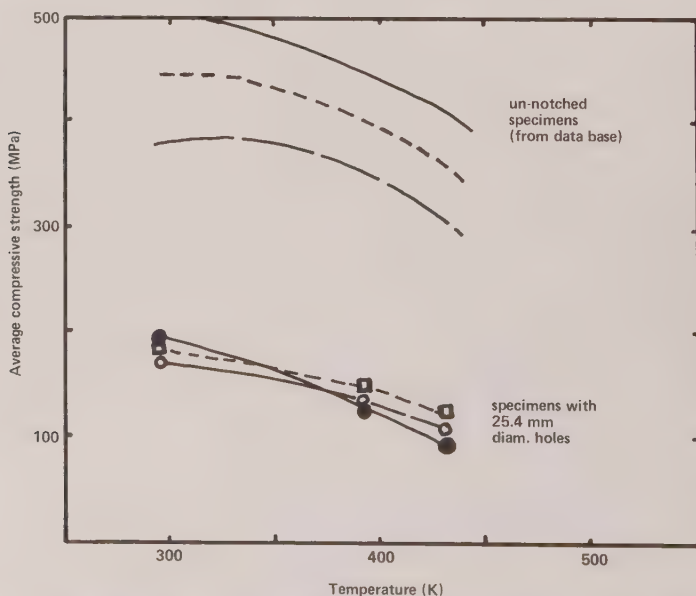


FIG. 2.8 The effect of 25.4 mm holes on the compressive strength of carbon-cloth/epoxy laminates. —●— $[0]_{4s}$; ---□--- $[0/45/0]_{2s}$; —○— $[0/45]_{2s}$.³¹

strength was invariably reduced and failure analysis showed extensive delamination, particularly with unidirectional samples. X-ray pictures showed the damage zone to be of the same magnitude as the hole diameter.³¹

The mutual adhesion of glass layers in polyester-glass laminates can be weakened if wax or wax-like substances are incorporated as trace additives into the matrix. Recently, the levels of wax additives have been increased, as a result of commercial demand for low volatility resins.³² The weakening effect is most noticeable if a laminate is made from a resin containing a wax with a tendency to separate out during storage, but slight weakening has also been suspected when multi-ply laminates are made in stages, with time intervals during which wax could migrate and concentrate at the surface — to which subsequent plies are supposed to adhere. The migration of radiotracer wax compounds in resins and laminates has been studied by Fifield *et al.*,³³ using ^{14}C -labelled hexadecane ($\text{C}_{16}\text{H}_{34}$) and pentacosane ($\text{C}_{25}\text{H}_{52}$). The evidence tended to suggest that waxes do not migrate to fibre-resin interfaces to any great extent, although they do to laminate surfaces (see Fig. 2.9). Mechanical



FIG. 2.9 Autoradiograph of a polyester/woven roving glass laminate containing ^{14}C -labelled pentacosane wax. The wax shows dark images (see also ref. 33).

property measurements by Haig *et al.*³⁴ suggest that the short-beam shear strength of laminates is hardly affected, but the ease of delamination by high speed impact with shear loading is increased for some resin-wax combinations. The use of a reactive adhesion promotor can minimise this problem.

2.8 VOIDS

2.8.1 Origin of Voids

Six causes of void generation can be distinguished, as follows:

- (1) Dissolved air within the resin.
- (2) Stirred-in (entrapped) air in the resin.
- (3) Entrapped air in filament bundles, inadequately impregnated.
- (4) Residual solvent carrier.
- (5) Reaction products from the curing process.
- (6) Volatilisation of low molecular weight components of the resin, or of organic inclusions at high cure temperatures.

Resin viscosity, moulding pressure and/or use of vacuum can be important parameters in the control of voids. The development of porosity in SMC is a special case and is believed to be caused by interaction between the thermosetting and thermoplastic components.³⁵

2.8.2 Measurement of Void Content and Distribution

Assessment of the void content of a laminate requires a knowledge of overall void volume fraction, V , void size distribution and void location. Some methods of determining V give an indication of the location of the larger voids, while others simply give an average value.

The most widely used is probably the *density method*, which assumes that $V = 1 - (V_f + V_r)$, where $V_f = W_f \cdot \rho_c / \rho_f$ and $V_r = (\rho_c / \rho_r)(1 - W_f)$ where W and ρ are weight fraction and density, respectively. The subscripts c, f and r refer to composite, fibre and resin, respectively.

The method is difficult and sometimes gives negative answers. The problems are these:

- (1) Very accurate determination of ρ_c , ρ_f , ρ_r and W_f is required.
- (2) Only small samples of material, not necessarily representative, can conveniently be used for determining ρ_c and W_f .
- (3) There is sometimes a polymeric coating on the fibres, of different density from that of the resin.

The determination of ρ_c can be carried out by means of a density gradient column filled with suitable liquids;³⁶ Ewins and Childs³⁷ recommend zinc chloride for carbon fibre composites. Measurement of W_f can be made either by ashing procedures (for glass fibre composites not containing other non-volatile additives) or by chemical methods. Carbon fibre composites can be treated by chemical oxidation of the resin matrix using concentrated sulphuric acid and 50% hydrogen peroxide.

Hussey's method³⁸ for the determination of ρ_f for carbon fibres uses a specific gravity bottle and bromobenzene as the immersion liquid.

Lenoe³⁹ and Olster⁴⁰ have calculated the effect of errors in density determination on the estimated void content. They conclude that 0.1% error in any of the parameters measured leads to an error of 2.5% in void content. In practice, errors can easily be made in excess of 0.1%.

The ultrasonic C-Scan technique measures the void content of a whole piece of laminate rather than a small sample of it, and is also non-destructive. Stone and Clarke⁴¹ have described the procedure for measuring the attenuation of a parallel beam, expressed in terms of unit thickness (dB/mm). Typical attenuation values are given in the literature. For example, laminates of carbon fibre reinforced with ERLA 4617 cured with DDM hardener were reported⁴² to have mean ultrasonic attenuations of 2dB/mm at the lowest void content ($\leq 1\%$) with a variation of ± 0.5 dB/mm. At 4.5% void content the mean attenuation rose to 10 ± 1 dB/mm. To distinguish between attenuation caused by voids and that caused by delamination, the back-echo from the latter defect has to be sought using a focused probe of frequency above 10 MHz.

Fibre volume fraction does not affect ultrasonic attenuation very much. Variations in degree of resin cure have some effect, but so long as the degree of cure is not grossly below par, this should not interfere with estimations of void content.

Ultrasonic estimations of voids have to be calibrated by reference to other methods of measurement and calibrations have to be repeated for each new fibre-resin combination.

The proposal that ultrasonic velocity, rather than attenuation, could be used in void determination has been discussed;⁴¹ the advantages lie with attenuation for most purposes.

Radiography has been used to determine void content. One approach is similar to that used for the study of craze microporosity in glassy thermoplastics.⁴³ Voids are impregnated with molten sulphur, and radiographed using a tungsten target.⁴⁴ Porosity can be detected down to 1 μm diameter. This method assumes that sulphur can reach and fill

all the voids, either because they are interconnected or because of activated diffusion.

Related techniques use radio-opaque penetrants of other kinds and also fluorescent dye penetrants. One of the disadvantages of all these methods is the time needed to permeate thick sections completely; attempts to accelerate the process by heating the specimen in hot aqueous liquids can introduce additional microcracks.

Optical micrography is useful for determining the general shape and the distribution of voids. Specimens are sectioned, polished and viewed under an optical microscope, fitted with a grid for counting purposes. This method examines only a small area at a time.

2.8.3 The Effect of Voids on Properties

The extent to which voids produce a deterioration in mechanical and other properties is a function of void content, void distribution and void shape. Common cavity shapes are spheres, ellipsoids, discs and fissures.

The majority of studies have been either experimentally based, without regard for distribution and shape, or theoretical computations with simplifying assumptions about these parameters. The effect of voids on impact strength is probably very dependent on void geometry.

According to Judd and Wright,⁴⁵ voids reduce the magnitude of the following mechanical properties:

- (1) Interlaminar (short beam) shear strength.
- (2) Longitudinal and transverse flexural strength and modulus.³⁹
- (3) Longitudinal⁴⁶ and transverse tensile strength and modulus.
- (4) Compressive strength⁴⁷ and modulus.
- (5) Fatigue resistance.^{46,47}

Also, high temperature durability can be impaired, together with certain electrical properties, and water absorption increases. An increase in impact strength has been observed.⁴⁸

Of all these properties, the one most extensively investigated is interlaminar shear strength, τ . An early theory of Greszczuk⁴⁹ derived the expression

$$\tau = \tau_{\max} \left[1 - \frac{\pi}{4} \left(\frac{6V}{\pi(1-V_f)} \right)^{2/3} \right]$$

for the case where spherically shaped voids were arranged in a cubic

array. $\tau_{\max}$ = shear strength when $V=0$. Another expression, i.e.

$$\tau = \tau_{\max} \left[1 - \left(\frac{4V}{\pi(1-V_f)} \right)^{1/2} \right]$$

was derived for cylindrical voids in a cylindrical array. The expression for spherical voids has been found to agree with experimental data. Most of the experimental observations suggest that a reduction of about 7% in τ is caused by each 1% void content, up to 4% voids. Cylindrical voids were found to be more effective in reducing τ .

Corten's theory⁵⁰ assumed that the voids could be regarded as small cracks and that the equivalent crack length was proportional to $V^{1/3}$. His equation related the critical stress intensity factor, K_{IIC} , to the shear strength and void content, i.e.

$$K_{IIC} \simeq C\tau V^{1/6}$$

Pritchard *et al.* measured the values of the short beam shear strength for some carbon-epoxy laminates as a function of void content before and after immersion for 13 weeks in various fluids.⁵¹ Table 2.1 gives some of the results obtained for the unimmersed laminates.

TABLE 2.1
VOID CONTENT AND SHEAR STRENGTH MEASUREMENTS FOR CARBON-EPOXY LAMINATES

W_f	Void content (by C-Scan) (%)	Void content (by density) (%)	Short beam shear strength (MPa)
0.56	0.7-1.0	0.6-0.9	77.0
0.54-0.56	0.9-1.1	0.2-0.8	76.5
0.49-0.50	1.0-1.2	0.7-0.8	77.1
0.49	1.3-5.0	2.6	68.8

Only rather large void contents reduced τ significantly. After immersion in various lubricating oils, fuels and anti-icing fluids, the shear strength values remained remarkably similar, sometimes increasing slightly.

Voids are believed to affect compressive strength adversely. Foye⁵² derived an expression for the shear modulus, G , in terms of $G_{\max}$, its

value when $V=0$. He concluded that

$$G = G_{\max} \cdot \frac{(R-1)^2}{(R+1)}$$

where $R = (V/1 - V_f)$. The predicted reduction in shear modulus could be related to compressive strength changes.

Pritchard and Tuck-Martin⁵³ introduced a regular array of small cylindrical voids into a cast resin block (otherwise essentially void free) and measured the effect of void geometry (at a constant 2.7% total void content) on the rate of transmission of water through the resin. The voids were of three different aspect ratios. The permeability of the voided sheet at 50°C was on average 17% higher than that of void-free resin sheets, but the experimental scatter was high and the effect of aspect ratio unclear.

Fried *et al.*⁵⁴ found that whereas the rate of water diffusion into laminates of low void content was very little affected by hydrostatic pressure, the water absorption characteristics of high-void laminates were decidedly pressure dependent, presumably because of the existence of capillaries for Poiseuille flow.

2.9 FAULTS DEVELOPING DURING SERVICE

2.9.1 Mechanical Damage

Stellbrink⁵⁵ has discussed mechanical damage by impact. When a hard object strikes a laminate, the energy absorbed depends on the relative velocity of the projectile and the laminate. The important question to consider is the nature and extent of the damage done by the collision and the effect of this damage zone on the subsequent behaviour of the laminate.

The effect of relatively low energy impacts on glass-resin composites with good interfacial bonding is to induce local fibre cracking, but if the interface is weak, interlaminar and intralaminar debonding occur. The size of the damage zone is linearly related to kinetic impact energy. Stellbrink found that small damage zones did not greatly affect the tension fatigue behaviour of either glass or carbon fabric reinforced materials, but there was evidence of a deterioration in the fatigue performance of 0°/90° carbon lay-ups, which were defect sensitive in tension. Multidirectional lay-ups were not affected so much. Under dynamic loading, the 0°/90° laminates lost the edge corners of the upper

0° layer, because the 90° layers prevented transverse contraction. The cracks eventually developing ran through the impact defects.

Defect-containing laminates also showed cracks parallel to the fibre direction, with some splitting of the outermost damaged lamina and partial delamination. This splitting also occurred in multidirectional ($0_2/\pm 45/0_2/\pm 45/90$)_s laminates.

The multidirectional lay-up, being better able to withstand in-plane shear stresses, was less notch sensitive in tension than the 0°/90° lay-up.

Impacted zones were about 10 cm² in area, and the damage consisted mainly of delamination; these zones could withstand tension much better than compression. Williams and Doll⁵⁶ have correlated ultrasonic attenuation above 1.5 MHz with fatigue lifetime. Bailey *et al.*⁵⁷ examined 16-ply graphite-epoxy laminates which had been fatigue cycled. The laminates were impacted by dropping a 1-lb (454 g) weight from 1.28 m height on to a 16.9 mm diameter indenter resting on the specimens. (Two were impacted before, and three after fatigue cycling.) Acoustic emission tests during tensile loading showed that the number of acoustic emission events increased with the number of fatigue cycles, and signals began with resin cracking at low (20% of ultimate) loads. Undamaged areas were very quiet in comparison with the damaged zones. The Kaiser effect did not hold for these zones.

Free-edge delamination and transverse cracking during uniaxial extension have recently been analysed by Wang.²⁸ Both these processes were discussed in terms of fracture mechanics, i.e. by comparing the calculated energy release rate (G_{calc}) with the material's critical strain energy release rate G_c , determined by stable crack growth experiments. If G_{calc} exceeds G_c , crack growth takes place. In many cases, the sites of likely delamination could be predicted. Onset strains for transverse cracking and for edge delamination were calculated, and the results were found to agree closely with experimental results. G_{calc} was calculated by a finite-element procedure.

De Charentenay and Benzeggagh⁵⁸ have studied the fracture mechanics of mode-I (cleavage) delamination in several materials including carbon-epoxy, aramid-epoxy and glass-polyester composites. Semi-log plots of the increase in fracture energy as a function of crack length showed clear transition points defining the boundary between micro-cracking and the onset of macroscopic delamination. (See Fig. 2.10 for the carbon-epoxy case; A_0 value refers to defect length in mm.)

Dingle *et al.* investigated the effect of sub-millimetre defects such as surface scratches, tiny holes and notches on the flexural strength of

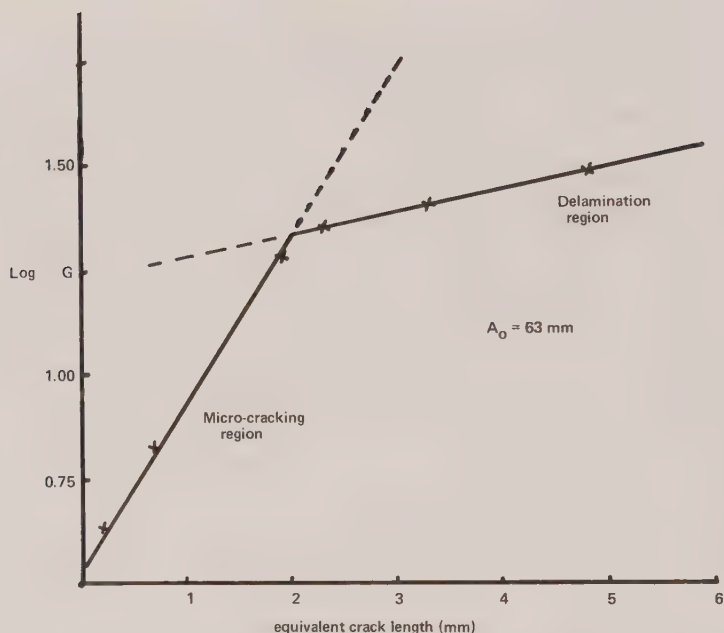


FIG. 2.10 Fracture energy as a function of crack length in carbon-epoxy laminates.⁵⁸ (Units of G , J/m².)

discontinuous, unidirectional, surface-treated high modulus carbon/Shell DX 210 epoxy/BF₃ material.⁵⁹ The results are summarised in Fig. 2.11; dotted lines show standard deviations. Substantial weakening was observed. For continuous high strength carbon fibre composites, the effect of notches was more severe than that of holes, but the weakening was similar for both defects in all other carbon composites. It should be noted, however, that both the strength and the notch sensitivity of CFRP have recently been improved considerably.

2.9.2 Fluid-induced Defects

The action of aqueous fluids on fibrous composites has been reviewed elsewhere by this author.⁶⁰ The special case of osmosis is of interest because it is by this means that internal, disc-shaped cavities are introduced into polyester resins and to a lesser extent, laminates. The formation of these disc cracks was probably first described in detail by Steel,⁶¹ who found that the rate of formation in castings was temperature

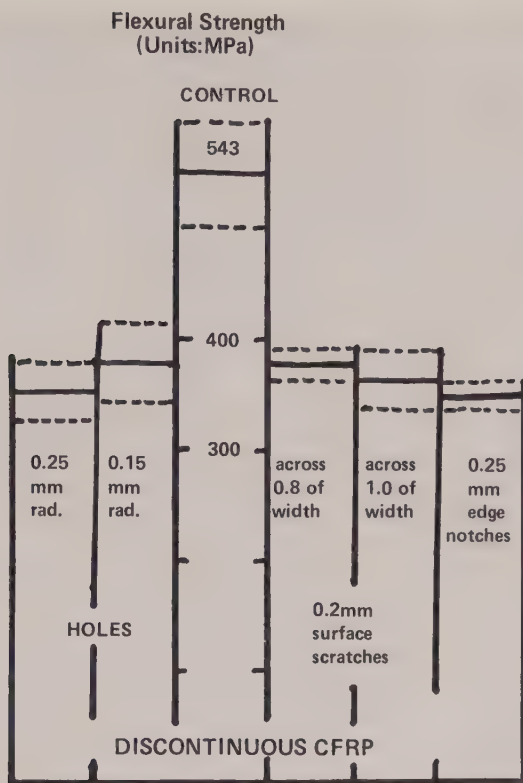


FIG. 2.11 Reduction of the flexural strength of carbon-epoxy laminates by defects such as holes, notches and surface scratches.⁵⁹

dependent, in accordance with an Arrhenius relationship. The rate of formation in laminates was said to be a function of the interstitial resin volumes between fibres.

The reason for disc crack formation was later provided by Ashbee *et al.*,⁶² who explained it as an osmotic process, in which water was attracted to inorganic water-soluble impurity sites within the matrix. Abeysinghe and Pritchard⁶³ demonstrated that the most active water-soluble impurity in polyesters was the organic reagent, residual glycol.

Figure 2.12 shows typical disc cracks in a casting after immersion in hot water. It is noticeable that their appearance is delayed by dissolved solute in the water, and that if the conditions favour a long incubation time, the cracks appear first within the body of the casting, while with



FIG. 2.12 Randomly oriented disc cracks in polyester castings after prolonged immersion in hot aqueous liquid. The crack-free region was the only part of the specimen edge directly in contact with water, and the soluble impurities leached out from this region long before cracks appeared. At very much longer immersion times, a few cracks appeared in this region also.⁶⁴

short incubation periods they appear first at the edge. The reason is probably that the phase-separated glycol tends to diffuse out of the specimen edges after a time.⁶⁴

Nicholas and Ashbee⁶⁵ investigated the generation of defects in fibre-resin laminates by the freezing or boiling of phase-separated water absorbed into the laminates. (Water in laminates is present partly as bound molecules, but it also fills voids, cracks and debonded interfaces.)

Samples of polyester and epoxy-glass laminates were immersed in water at 80°C to allow for water absorption, and then cooled in a freezing mixture to -95°C. Disc-shaped resin cracks were observed. Some of these cracks were attributed to the osmotic process just discussed, and were assumed to have been formed during immersion. The remainder were believed to have grown during the freezing process, since the stresses induced by expansion of water on freezing were estimated to be three or four times the resin tensile strength.

When similar samples were placed in an oven at 200°C, or in an oxygen-coal gas flame, large scale inhomogeneous flow was observed. Pure water should boil and generate very large stresses, but dilute solutions simply exert increasing osmotic pressures, and no cracking was to be expected because the resins were above their glass transition temperatures.

Osmotic pressure also generates blisters in polyester-glass laminates exposed to warm water.⁶⁶ The water-soluble impurities responsible are believed to originate in both the resin and the glass. The process of blistering is slow in cold water, and usually of cosmetic importance only, but large or deep-lying blisters can expose underlying reinforcement, and may eventually require repair. A blistered panel is shown in Fig. 2.13.

The absorption of fluids by laminates and subsequent desorption by

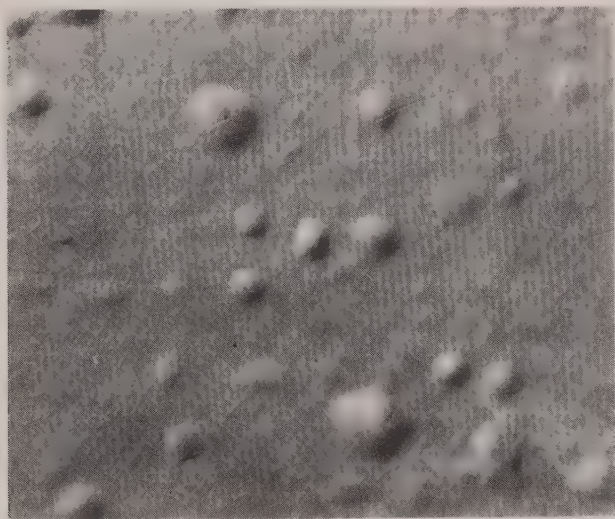


FIG. 2.13. Osmotic blistering under the gelcoat of a polyester-glass laminate.

drying can produce irreversible damage in high crosslinked resins. Debonding, resin microcracking and glass damage are all thought to occur. Resin-rich regions between filament bundles are sites for disruptive swelling stresses.

2.9.3 The Repair of Defects

Some of the defects discussed above can be repaired, while others cannot. The repair of blister-damaged gelcoats has been described in a recent guide⁶⁷ and Lubin⁶⁸ gave details of procedures for the repair of boron-epoxy structures, known to be severely weakened by small holes. These techniques included the insertion of tapered titanium plugs, adhesively bonded to the laminate; and also the use of a tapered lap joint, employing several layers of titanium foil as well as fibre-glass. The strength of a repaired FRP component can be slightly or considerably less than that of the original, and repaired sections must be free from sharp projections in order to approach the desired strength recovery values. Titanium is particularly convenient for isotropic boron-epoxy laminates, since it has similar strength and stiffness.

Kiger and Back⁶⁹ discussed the repair of large areas of defective FRP to aerospace standards. Several joint concepts, capable of giving good recovery of original mechanical properties, were outlined. Major repairs to damaged GRP structures are described by Joest *et al.*⁷⁰

2.10 CONCLUSIONS

The properties of reinforced plastic materials depend upon the quality of the particular sample being evaluated. In this respect, they are like other materials; the only difference is the precise origin and nature of the defects which detract from optimum performance.

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Chapter 3

MOISTURE ABSORPTION IN FIBRE-RESIN COMPOSITES

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SUMMARY

A survey is presented of the effects of moisture and temperature on the moisture absorption and desorption characteristics of fibre reinforced organic matrix composites. Expressions and analytical methods are given for calculating (in the case of Fickian diffusion) temperature and moisture distributions and moisture content as a function of time in single and multilayered composites exposed both to steady and to transient ambients. The main features of non-Fickian moisture transport processes are described. The changes in glass transition temperature with moisture content and changes in absorption-desorption behaviour during exposure to cyclical environments are also discussed.

3.1 INTRODUCTION

Owing to their favourable performance characteristics, fibre reinforced organic matrix composites have been gaining wide use in commercial, space and military applications. There is some concern, however, that the performance of such materials may suffer during long-term exposure to high moisture content and high temperature environments. Therefore, in

order to utilize the full potential of composite materials their response to absorbed moisture and elevated temperatures must be known. Moisture absorbed by the material increases its weight. Absorbed moisture and an increase in temperature result in changes in the structure and mechanical properties of the material. It is for these reasons that the designer seeks to determine the variation with time of the moisture content and the temperature of the material. Specifically, answers to the following problems are sought.

A composite material is exposed to an environment in which the temperature and moisture content vary in a prescribed manner. It is required to find the following parameters:

- (a) The temperature inside the material as a function of position and time.
- (b) The moisture concentration inside the material as a function of position and time.
- (c) The total amount (mass) of moisture inside the material as a function of time.

In this chapter a survey is given of the available analytical methods and test results pertaining to the problem stated in the foregoing. Attention will be focused on practical methods and approaches which might be useful in actual applications of composite materials. Solutions and data are not presented in detail. Additional details may be found in the appropriate references.

3.2 PROBLEM STATEMENT

A problem in which the temperature and moisture distributions inside a material are to be determined is frequently referred to as a 'moisture problem'. Answers to such problems can be obtained by analytical means when the following conditions are met:

- (a) Heat transfer through the material is by conduction only and can be described by Fourier's law.
- (b) The moisture diffusion can be described by a concentration-dependent form of Fick's law.
- (c) The temperature inside the material approaches equilibrium much faster than the moisture concentration and hence the energy (Fourier) and mass transfer (Fick) equations are decoupled.

- (d) The thermal conductivity and mass diffusivity depend only on temperature and are independent of moisture concentration or stress levels inside the material.

When all the foregoing assumptions are satisfied the diffusion process is said to be 'Fickian'. In the case of Fickian diffusion, the temperature and moisture distributions inside the material can be calculated according to the procedures outlined in the following sections.

3.3 ANALYSIS — FICKIAN DIFFUSION

Consider a composite material surrounded by a fluid (Fig. 1). The temperature and the moisture content of the ambient, denoted by T_a and c_a respectively, vary with position $\mathbf{r}$ and time t in a specified manner.

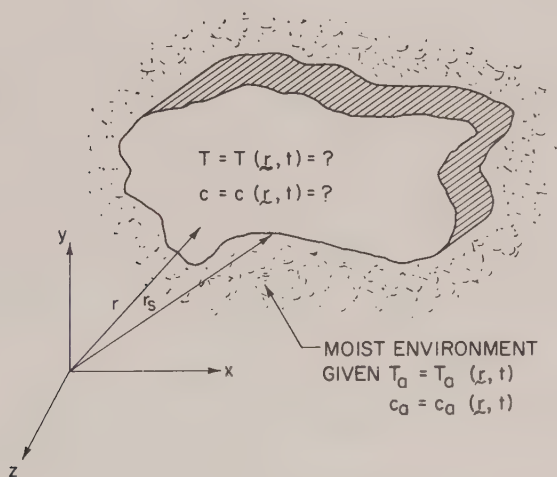


FIG. 3.1 Description of the problem.

Thus the following conditions exist in the ambient:

$$\begin{aligned} T_a &= T_a(\mathbf{r}, t) & \mathbf{r} &= \mathbf{r}_s \\ c_a &= c_a(\mathbf{r}, t) & \mathbf{r} &= \mathbf{r}_s \end{aligned} \quad (1)$$

The initial (time $t=0$) temperature and moisture content of the material (denoted by T_i and c_i) are also known. Both T_i and c_i may vary with

position:

$$\begin{aligned} T_i &= T_i(\mathbf{r}) & t &= 0 & \mathbf{r} < \mathbf{r}_s \\ c_i &= c_i(\mathbf{r}) & t &= 0 & \mathbf{r} < \mathbf{r}_s \end{aligned} \quad (2)$$

The problem at hand is to determine the temperature T and the moisture concentration c inside the material as a function of both position and time, and the total moisture content of the material as a function of time.

In most materials the temperature and the moisture diffusion processes can be described adequately by the Fourier equation:¹

$$\rho C \frac{\partial T}{\partial t} = \nabla \cdot (\mathbf{K} \cdot \nabla T) \quad (3)$$

and by the Fick equation:²

$$\frac{\partial c}{\partial t} = \nabla \cdot (\mathbf{D} \cdot \nabla c) \quad (4)$$

where ρ is the density, C the specific heat, $\mathbf{K}$ the thermal conductivity and $\mathbf{D}$ the diffusivity of the material. For anisotropic materials (such as fibre reinforced composites) $\mathbf{K}$ and $\mathbf{D}$ are second rank tensors and their values depend on the orientation. In order to obtain solutions to eqns. (3) and (4) the initial and boundary conditions must be specified. The initial conditions are given by eqn. (2). The boundary conditions which must be known are the temperature and the moisture concentration on the surface of the material. The surface temperature may be taken to be the same as the temperature of the ambient

$$T = T_a(t) \quad \mathbf{r} = \mathbf{r}_s \quad t > 0 \quad (5)$$

The moisture concentration at the surface of the material is denoted by c_m

$$c = c_m(t) \quad \mathbf{r} = \mathbf{r}_s \quad t > 0 \quad (6)$$

where c_m is the maximum moisture concentration that is reached in the material for a given ambient condition. Thus, for a given material, c_m depends on the ambient moisture concentration c_a and on the ambient temperature T_a .

For multilayered materials, two more conditions must be specified at the interface of each layer.^{3,4}

(a) The masses of moisture crossing the surface of two adjacent layers

per unit area and unit time are equal

$$\left[D_n \frac{\partial c}{\partial n} \right]_{\text{left layer}} = \left[D_n \frac{\partial c}{\partial n} \right]_{\text{right layer}} \quad (7a)$$

(b) The moisture concentrations at the surfaces (denoted by c_m) of two adjacent layers correspond to the same relative humidity, ϕ

$$[c_m]_{\text{left layer}} \rightarrow \phi \leftarrow [c_m]_{\text{right layer}} \quad (7b)$$

where D_n is the diffusivity normal (n direction) to the surface.

In order to obtain solutions to the problem described by eqns. (1)–(7) the following parameters must be known:

- (a) Geometry (material thickness in one-dimensional problems).
- (b) Boundary conditions: ambient temperature and moisture content.
- (c) Initial conditions: temperature and moisture concentrations inside the material.
- (d) Material properties: density ρ , specific heat C , thermal conductivity K , mass diffusivity D , maximum moisture content c_m and a relationship between the maximum moisture content and the ambient conditions.

Solutions to eqns. (1)–(7) can be obtained using simplifying assumptions. Some of these solutions are discussed in the following sections:

3.3.1 Single Layer Composite—Constant Boundary Conditions

Simple, closed-form solutions to eqns. (1)–(7) may be obtained by the following simplifying assumptions:

- (a) The composite is a single-layer plate in which the moisture content and temperature vary only in the direction normal to the face of the plate (i.e. the problem is one-dimensional, parameters vary in the x -direction only, Fig. 3.2).
- (b) The ambient temperature and ambient moisture content are constant and are the same on both sides of the plate.
- (c) The temperature inside the material approaches equilibrium much faster than the moisture concentration and hence the temperature inside the material can be taken to be the same as the ambient temperature.
- (d) Initially, the temperature and moisture distributions are uniform inside the material.
- (e) The thermal conductivity and the mass diffusivity depend only on

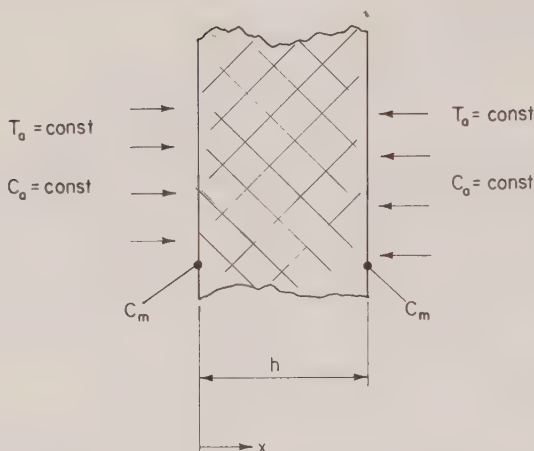


FIG. 3.2 Single layer composite—constant boundary conditions.

temperature and are independent of moisture concentration and the stress levels inside the material.

- (f) The plate is made of a single layer only and the material is quasihomogeneous, so that variations of ρ , C , K_x , and D_x with position inside the material may be neglected. (N_x and D_x are the thermal conductivity and mass diffusivity in the direction normal to the face of the plate.)

The latter two assumptions imply that ρ , C , K_x and D_x depend only on temperature, but are independent of time and position.

For the above assumptions the temperature inside the material is uniform and constant

$$T_i = T_a = T \quad 0 \leq x \leq h \quad t \geq 0 \quad (8)$$

and the concentration is described by the equation

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \quad (9)$$

and the initial and boundary conditions

$$c = c_i \quad 0 \leq x \leq h \quad t < 0 \quad (10a)$$

$$c = c_a \quad x < 0; x > h \quad t \geq 0 \quad (10b)$$

The solution of eqns. (9) and (10) is

$$c^* \equiv \frac{c - c_i}{c_m - c_i} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{1}{2j+1} \sin \frac{(2j+1)\pi x}{h} \exp \left[-\frac{(2j+1)^2 \pi^2 D_x t}{h^2} \right] \quad (11)$$

The total mass of moisture in the material is obtained by integrating eqn. (11) over the plate thickness

$$m = A \int_0^h c \, dx \quad (12)$$

where A is the exposed surface area. The result of the integration is

$$G \equiv \frac{m - m_i}{m_m - m_i} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp \left[-(2j+1)^2 \pi^2 \left(\frac{D_x t}{h^2} \right) \right]}{(2j+1)^2} \quad (13)$$

where m_i is the initial mass of the material (that is, the mass prior to exposure to the moist environment) and m_m is the mass of moisture in the material when the material is fully saturated, in equilibrium with its environment.

A parameter of practical interest is the per cent weight gain, defined as

$$M = \frac{\text{weight of moist material} - \text{weight of dry material}}{\text{weight of dry material}} \times 100 \quad (14)$$

$$M = \frac{W - W_d}{W_d} \times 100 = \frac{m - m_d}{m_d} \times 100$$

The total weight of the material is equal to the sum of the dry weight W_d and the weight of the absorbed moisture

$$W = W_d + (m/g) \quad (15)$$

The subscripts i and m refer to the uniform initial and fully saturated conditions, respectively. Equations (13)–(15) give

$$M = G (M_m - M_i) + M_i \quad (16)$$

Note that c_m and M_m are related in a unique manner (see eqns. 12–14). Once c_m is known, M_m can be calculated. On the other hand c_m can be determined from the known value of M_m .

3.3.2 Multilayered Composites — Transient Boundary Conditions

Equations (1)–(7) may be applied to multilayered composites with time-dependent boundary conditions (Fig. 3.3). In this case, closed form solutions cannot be obtained and results must be generated by numerical methods. A computer program for solving such problems (designated as

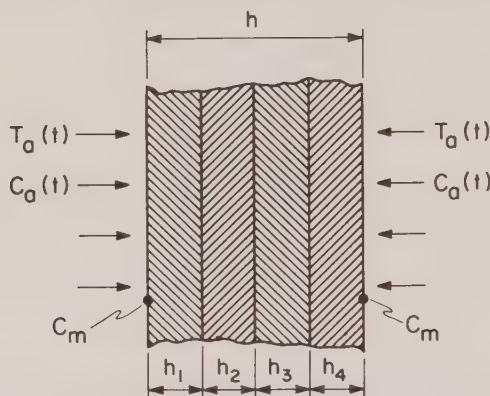


FIG. 3.3 Multilayered composites—transient boundary conditions.

w8GAIN) was developed in the Fluid Dynamics Laboratory, Department of Mechanical Engineering, of The University of Michigan. This program is based on the following approximations:

1. The problem is one-dimensional.
2. The temperature inside the material equilibrates much faster than the moisture concentration, and hence at each instant of time the temperature distribution inside the material corresponds to the instantaneous ambient temperature.
3. The material properties ρ , C , K_x and D_x depend only on temperature, being independent of moisture concentration and stress level.

The required input parameters for the program are:

- (a) The ambient temperature and moisture content as a function of time on both sides of the plate.
- (b) The initial moisture concentration and initial temperature distribution inside the plate; these concentrations need not be uniform.
- (c) The density of each layer.
- (d) The maximum moisture content of each layer as a function of ambient conditions.

- (e) The thermal conductivity and mass diffusivity as a function of temperature for each layer.

The outputs of the program are:

- (a) Moisture concentration as a function of position and time in each layer.
- (b) Weight (mass) change of each layer as a function of time.
- (c) Total weight (mass) change as a function of time.

A description of the data input cards, listing of the `w8GAIN` program and a sample input-output are given in ref. 4.

3.4 CONSTANTS REQUIRED IN THE ANALYSIS

Solutions to eqns. (1)–(16) can be obtained only if the material properties ρ , C , $\mathbf{K}$, $\mathbf{D}$, and c_m are known.

All these properties depend on the material, on the temperature and (with the exception of c_m) on the amount of absorbed moisture. The moisture inside the material makes the measurement of these properties extremely difficult. It is commonly assumed, therefore, that ρ , C , $\mathbf{K}$ and $\mathbf{D}$ are not affected significantly by the amount of moisture, and the dry material values of these properties are used in the calculations. There is some experimental evidence that this assumption is reasonable.⁴⁻⁶

The density and the specific heat of the material are generally known. The problem is to determine the values of $\mathbf{D}$, c_m and $\mathbf{K}$.

It is noted here that in some problems the heat and moisture transport may be coupled, and the two processes cannot be treated independently. In this case additional material constants are required in the solution. Unfortunately, it is extremely difficult to deduce these constants from tests and, therefore, presently the values of these constants are unknown.² In the absence of these constants the results of coupled heat and moisture diffusion theories (e.g. see ref. 2) cannot be applied to practical problems.

3.4.1 Test Procedures for Determining $\mathbf{D}$ and c_m (or M_m)

The following test procedure may be used to determine $\mathbf{D}$ and c_m :

- (a) A test specimen is made in the form of a thin plate (thickness h), so that moisture enters predominantly through the face (not the edges) of the plate.

- (b) The specimen is completely dried in a desiccator and its dry weight W_d is measured.
- (c) The specimen is placed in a constant temperature, constant moisture environment and its weight W is recorded as a function of time.
- (d) The moisture content (per cent weight gain) $M = (W - W_d)/W_d$ is plotted versus $\sqrt{t}$, as illustrated in Fig. 3.4.
- (e) The tests are repeated for different temperatures and different environmental moisture contents.

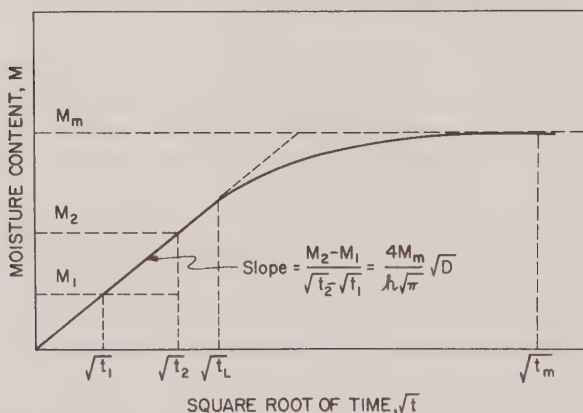


FIG. 3.4 Illustration of the change of moisture content with the square root of time for Fickian diffusion. For $t < t_L$ the slope is constant.

The above procedure yields a series of curves similar to the one shown in Fig. 3.4. Initially (when $t < t_L$, Fig. 3.4) all curves are straight lines, the slope being proportional to the diffusivity of the material. After a long period of time the curves approach asymptotically the maximum moisture content M_m . The value of M_m is a constant when the material is fully submerged in a liquid; it varies with the relative humidity when the material is exposed to humid air.

The diffusivity D is obtained from the initial slope ($t < t_L$) of the M versus $\sqrt{t}$ curve (refs. 4 and 5)

$$D = \pi \left(\frac{h}{4M_m} \right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (17)$$

If the moisture entering the specimen through the 'edges' can be

neglected D_x is

$$D_x = D \quad (18)$$

A procedure for estimating the influence of edge effects is given in refs. 4 and 5. The foregoing procedure requires that each specimen be tested until the maximum moisture content is reached ($t = t_m$). The tests may be accelerated by the method outlined in refs. 4 and 5.

3.4.2 Maximum Moisture Content M_m

For a given material, the maximum moisture content depends on the temperature and moisture content of the environment. For materials exposed to humid air the maximum moisture content seems to depend on the relative humidity, ϕ , in the following manner:

$$M_m = a\phi^b \quad (19)$$

where a and b are constants. At first b was believed to range from 1 to 2. Recent experimental evidence suggests that the value of b is near unity.^{4,7} The above relationship is only an approximation, introduced for the purpose of computations. In fact, M_m varies with temperature. Twenty percent variations in M_m with temperature are common.

In many situations, changes in the value of M_m have been observed after the maximum, asymptotic value of M_m has been reached. Both increases and decreases in M_m have been noticed. The increase in M_m is due to cracks developing in the material and, possibly, to non-Fickian diffusion (see Section 3.5). The decrease in M_m may be caused by loss of material due to leaching or cracking. When M_m does not depend uniquely on the material and on the ambient moisture content, the results of the calculations described in Section 3.3 become invalid.

The values of M_m have been measured for several materials under a wide range of environmental conditions. These conditions include exposure of materials to humid air as well as to various liquids. A summary of the data is presented in Tables 3.1, 3.2 and 3.3.

3.4.3 Mass Diffusion Coefficient (Diffusivity), D .

The mass diffusion coefficient (diffusivity) characterizes the speed at which moisture is transported through the material. The value of D depends on the material, on the fluid surrounding the material, on the moisture concentration inside the material, on the stress level inside the material and on the temperature. Unfortunately, there are few data

TABLE 3.1

MAXIMUM MOISTURE CONTENTS OF SELECTED GRAPHITE-EPOXY COMPOSITES
IMMERSED IN LIQUID^{4,7}

Liquid	Maximum moisture content, M_m (%)		
	T300/1034	AS/3501-5	T300/5208
Distilled water	1.70	1.90	1.50
Saturated salt water	1.25	1.40	1.12
No. 2 Diesel fuel	0.50	0.55	0.45
Jet A fuel	0.45	0.52	0.40
Aviation oil	0.65	0.65	0.60

TABLE 3.2

MAXIMUM MOISTURE CONTENTS OF SELECTED GRAPHITE-EPOXY COMPOSITES
AND EPOXY RESINS EXPOSED TO HUMID AIR, $M_m = a\phi^b$ WHEN $b = 1$;
 $M_m = a(\phi/100)^b \times 100$ WHEN $b \neq 1$.^{4,7}

Material	Investigator	a	b
T300/1034	Loos-Springer ⁷	0.017	1
	Shen and Springer ^{4a}	0.014	—
	Bohlmann and Derby ^{8a}	0.018	—
AS/3501-5	Loos-Springer ⁷	0.019	1
	DeIasi and Whiteside ⁹	0.0186	1.6, $\phi < 60\%$ 1.9, $\phi > 60\%$
	Whitney and Browning ¹⁰	0.016	1.1
T300/5208	Loos-Springer ⁷	0.015	1
	Shirrell ¹¹	0.0155	1
	McKague <i>et al.</i> ¹²	0.0146	1
	Husman ¹³	0.0150	1.81
934 (neat resin)	DeIasi and Whiteside ⁹	0.063	1.4, $\phi < 60\%$ 1.8, $\phi > 60\%$
	Augl and Berger ^{6a}	0.049	—
3501-5 (neat resin)	DeIasi and Whiteside ⁹	0.063	1.4, $\phi < 60\%$ 1.8, $\phi > 60\%$
	Whitney and Browning ¹⁰	0.06	1.22
5208 (neat resin)	DeIasi and Whiteside ⁹	0.063	1.4, $\phi < 60^\circ$ 1.8, $\phi > 60^\circ$
	Augl and Berger ⁶	0.059	1
	McKague <i>et al.</i> ¹⁴	0.066	1.28

^aOne data point only.

TABLE 3.3
THE APPARENT MAXIMUM MOISTURE CONTENT OF SELECTED POLYESTER E-GLASS
AND VINYLESTER E-GLASS COMPOSITES (PER CENT)^{4,15,16}

Substance	Temperature (°C)	SMC-R25	VE SMC-R50	SMC-R50
Humid air, 50%	23	0.17	0.13	0.10
	93	0.10	0.10	0.22
Humid air, 100%	23	1.00	0.63	1.35
	93	0.30	0.40	0.56
Distilled water	23	3.60	—	—
	50	3.50	—	—
Salt water	23	0.85	0.50	1.25
	93	2.90	0.75	1.20
No. 2 diesel fuel	23	0.29	0.19	0.45
	93	2.80	0.45	1.00
Lubricating oil	23	0.25	0.20	0.30
	93	0.60	0.10	0.25
Antifreeze	23	0.45	0.30	0.65
	93	4.25	3.50	2.25
Indolene	23	3.50	0.25	0.60
	93	4.50	5.00	4.25

available showing either the dependence of **D** on moisture concentration⁶ or on the imposed stresses.^{17,18} For this reason the moisture content inside the material is generally calculated with the assumption that **D** depends only on temperature. In many practical problems this is an adequate approximation. Evaluation of the dependence of **D** upon moisture concentration and upon the stress level merits further consideration.

When (a) the diffusion is Fickian, and (b) **D** is a function of temperature only, the diffusivity is related to temperature by the Arrhenius relationship

$$D = D_0 \exp \left[-\frac{E}{RT} \right] \quad (20)$$

where D_0 and R are constants, E is the activation energy and T is the absolute temperature. For fibre reinforced composites the diffusion coefficients in the direction parallel and perpendicular to the fibres (D_{11} and D_{22}) may be estimated by the expressions^{4,5} ($v_f < 0.785$)

$$D_{11} = (1 - v_f)D_r + v_f D_f \quad (21)$$

and

$$D_{22} = (1 - 2\sqrt{v_f/\pi})D_r + \frac{D_r}{B_D} \left[\pi - \frac{4}{\sqrt{1 - (B_D^2 v_f/\pi)}} \tan^{-1} \frac{\sqrt{1 - (B_D^2 v_f/\pi)}}{1 + B_D \sqrt{v_f/\pi}} \right] \quad (22)$$

$$B_D \equiv 2 \left(\frac{D_r}{D_f} - 1 \right)$$

where D_r is the diffusivity of the resin, D_f is the diffusivity of the fibre and v_f is the volume fraction of the fibres. Equations (21) and (22) are based on the assumption that moisture transport is by Fickian diffusion only. These expressions become invalid if moisture propagates along fibre-resin interfaces or through cracks and voids.

Generally, the diffusivity of the fibre is small compared to the diffusivity of the matrix ($D_f \ll D_r$) and eqns. (21) and (22) reduce to ($v_f < 0.785$)

$$D_{11} = (1 - v_f)D_r \quad (23)$$

$$D_{22} = (1 - \sqrt{v_f/\pi})D_r \quad (24)$$

In a direction making α degrees with the orientation of the fibres the diffusivity is²

$$D_\alpha = D_{11} \cos^2 \alpha + D_{22} \sin^2 \alpha \quad (25)$$

Note that in the direction parallel to the fibres $\alpha = 0^\circ$ and $D_\alpha = D_{11}$; in the direction perpendicular to the fibres $\alpha = 90^\circ$ and $D_\alpha = D_{22}$.

Diffusivities of different composites exposed to humid air and to various liquids have been measured. A summary of the data is given in Tables 3.4, 3.5 and 3.6.

TABLE 3.4
TRANSVERSE DIFFUSIVITIES OF SELECTED GRAPHITE EPOXY COMPOSITES
IMMERSED IN LIQUIDS^{4,7}

Liquid	T300/1034		AS/3501-5		T300/5208	
	D_0	C	D_0	C	D_0	C
Distilled water	16.3	6211	768	7218	132	6750
Saturated salt water	5.85	6020	5.38	6472	6.23	5912

The transverse diffusivity is $D_{22} = D_0 \exp(-C/T)$ where D_0 is in $\text{mm}^2 \text{s}^{-1}$ and C is in K.

TABLE 3.5
TRANSVERSE DIFFUSIVITIES OF SELECTED GRAPHITE EPOXY COMPOSITES AND
EPOXY RESINS EXPOSED TO HUMID AIR^{4,7}

Material	Investigator	$D_0(\text{mm}^2 \text{ s}^{-1})$	C(K)
T300/1034	Loos-Springer ⁷	2.28	5554
	Shen and Springer ⁵	0.44	5058
AS/3501-5	Loos-Springer ⁷	6.51	5722
	Whitney and Browning ¹⁰	0.44	4768
	DeIasi and Whiteside ⁹	28.8	6445
T300/5208	Loos-Springer ⁷	0.57	4993
	Augl and Berger ⁶	0.41	5231
934 (neat resin)	Shen and Springer ⁵	4.85	5113
	DeIasi and Whiteside ⁹	16.4	5992
3501-5 (neat resin)	DeIasi and Whiteside ⁹	16.1	5690
5208 (neat resin)	Augl and Berger ⁶	2.8	5116
	McKague <i>et al.</i> ¹⁴	0.051	4060
	DeIasi and Whiteside ⁹	4.19	5448

$$D_{22} = D_0 \exp(-C/T).$$

The effects of non-Fickian diffusion on the values of D are discussed in Section 3.5.

3.4.4 Thermal Conductivity, K .

The thermal conductivity is a measure of the speed at which heat is conducted through the material. For many composite materials K is 10^4 – 10^6 times larger than D . Thus, the temperature equilibrates much faster than the moisture concentration.

As in the case of diffusivity, the thermal conductivity may depend on the moisture concentration, on the stress level and on the temperature. And, as with diffusivity, the variations of K with moisture concentration and with stress are unknown. Thus, presently, calculations are performed by taking K to vary with temperature only.

The thermal conductivity of composites may be determined by tests or may be approximated from the known fibre and matrix properties^{4,19}

TABLE 3.6
APPARENT TRANSVERSE DIFFUSIVITIES OF SELECTED POLYESTER E-GLASS AND VINYLESTER E-GLASS COMPOSITES.

Substance	Temperature (°C)	SMC-R25	VE SMC-R50	SMC-R50
Humid air, 50%	23	10.0	10.0	30.0
	93	50.0	50.0	30.0
Humid air, 100%	23	10.0	5.0	9.0
	93	50.0	50.0	50.0
Salt water	23	10.0	5.0	15.0
	93	5.0	30.0	80.0
No. 2 diesel fuel	23	6.0	5.0	5.0
	93	6.0	10.0	5.0
Lubricating oil	23	10.0	10.0	10.0
	93	10.0	10.0	10.0
Antifreeze	23	50.0	30.0	20.0
	93	5.0	0.8	10.0
Indolene	23	1.0	10.0	10.0
	93	40.0	1.0	3.0

Values given are $D_{22} \times 10^7 \text{ mm}^2/\text{s}$.^{15,16}

($v_f < 0.785$)

$$K_{11} = (1 - v_f)K_r + v_f K_f \quad (26)$$

$$K_{22} = (1 - 2\sqrt{v_f/\pi})K_r + \frac{K_r}{B_K} \left[\pi - \frac{4}{\sqrt{1 - (B_K^2 v_f/\pi)}} \tan^{-1} \frac{\sqrt{1 - (B_K^2 v_f/\pi)}}{1 + B_K \sqrt{v_f/\pi}} \right] \quad (27)$$

$$B_K \equiv 2 \left(\frac{K_r}{K_f} - 1 \right)$$

where K_{11} and K_{22} are the thermal conductivities in a direction along the fibre ($\alpha = 0^\circ$) and perpendicular to the fibre ($\alpha = 90^\circ$). K_r and K_f are the thermal conductivities of the resin and the fibre, respectively. In the α direction¹

$$K_\alpha = K_{11} \cos^2 \alpha + K_{22} \sin^2 \alpha \quad (28)$$

3.5 NON-FICKIAN DIFFUSION

The fundamental characteristics of Fickian and non-Fickian behaviour were described by Crank.² Essentially, in Fickian diffusion, the absorp-

tion (weight gain) and desorption (weight loss) curves when plotted against $(\text{time})^{1/2}$ are always concave towards the $(\text{time})^{1/2}$ axis and asymptotically reach the final equilibrium value. Furthermore, when the diffusivity is a function of temperature only, then on a weight gain, M , versus $(D t/h^2)^{1/2}$ plot the absorption and desorption curves coincide. Calculations performed on the basis of Fick's law fail if:

- (a) Cracks develop in the material or delamination occurs, essentially altering the structure of the material.
- (b) Moisture propagates along the fibre-matrix interface.
- (c) There are voids in the matrix.
- (d) The matrix itself (even without cracks) exhibits non-Fickian behaviour.

The first three of these conditions involve some form of discontinuity inside the material. Frequently, such discontinuities can be minimized by appropriate manufacturing procedures. Non-Fickian behaviour (point d) is a material characteristic. Whether the diffusion process through the matrix is Fickian or non-Fickian depends on the relative rates at which the polymer structure and the moisture distributions change. When the polymer structure changes much faster than the moisture concentration the diffusion process can be described adequately by Fick's law. If relaxation processes inside the material progress at a rate comparable to the diffusion processes the diffusion is said to be non-Fickian or anomalous.

Fick's law is generally applicable to rubbery polymers but often fails to describe the diffusion process in glassy polymers. The transition from a glassy to a rubbery state occurs at the glass transition temperature (Section 3.6).

Experimental evidence indicates that for many materials (especially for graphite-epoxy composites) Fickian diffusion is a reasonable approximation.⁴ However, moisture absorption and desorption in some polymers proceeds by non-Fickian processes. The following are some of the main features of non-Fickian absorption-desorption processes:

- (a) Initially, for a short period of exposure time, the moisture absorption is nearly Fickian. However, the diffusion coefficient corresponding to this absorption process is only an 'apparent' diffusivity. It does not correlate with temperature according to the Arrhenius relationship, as in the case of Fickian diffusion (eqn. 20).

- (b) Beyond some exposure time the absorption process becomes non-Fickian. The rate of moisture uptake and the amount of moisture absorbed are generally less than the values predicted by Fick's law. Frequently, pseudo-Fickian absorption and 'two stage' absorption have been observed. In the former case the absorption curve is similar in character to the Fickian absorption curve, but the rate of absorption is slower. In the latter case two apparent maximum saturation levels are reached, as illustrated in Fig. 3.5. Occasionally, S-shape absorption curves have also been observed.

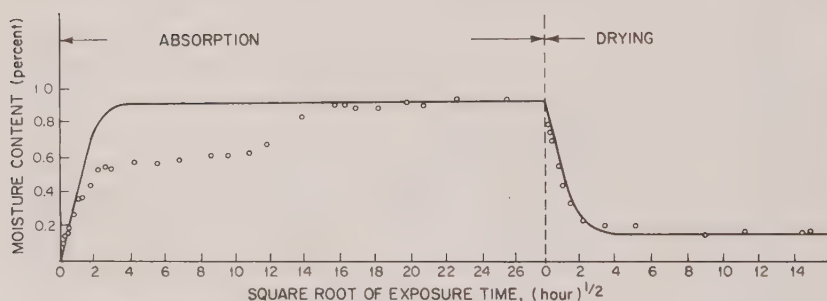


FIG. 3.5 Illustration of a two-stage absorption process. Circles are data for a glass fibre reinforced epoxy immersed in humid air (99% r.h., 75°C). Solid line is Fick's law solution with $D = 1 \times 10^{-6} \text{ mm}^2/\text{s}$ and $M_m = 0.9\%$.

- (c) A maximum saturation level is reached. However, the moisture content may not remain constant at this 'apparent' maximum level, but may decrease or increase as time progresses. This apparent maximum saturation level does not correlate with relative humidity as in the case of Fickian diffusion.
- (d) Subsequent drying and remoisturizing processes follow Fickian behaviour better than the first absorption process, provided the material does not become damaged excessively. Such damage is manifested by a steep increase followed by a steep decrease in the rate of change in the weight of the material. The increase in weight (and moisture content) is due to microcracks which develop in the material and which enable the moisture to diffuse into the material rapidly. At later times the weight of the material decreases due to the fact that material (resin) is lost at a faster rate than moisture is absorbed.

- (e) The material retains some moisture when dried after the first absorption process. After subsequent remoisturization and drying the retained moisture level appears to be nearly the same.

Whether or not moisture transport through a composite is by Fickian diffusion depends both upon the material and upon the environmental conditions. Graphite fibre reinforced epoxy matrix composites are more likely to conform to Fick's law than glass or Kevlar fibre reinforced polyester or vinylester composites. Equations based on Fick's law are more apt to describe the moisture transport at low temperatures and for materials exposed to humid air. Deviations from Fick's law solutions become more pronounced at elevated temperatures and for materials immersed in liquids. Salt water, solvents and hydrocarbons are especially detrimental to the material.

Whether or not Fick's law is applicable in a given situation can not be guessed '*a priori*' but must be determined by tests. Once it has been established that the diffusion is Fickian, the moisture history in the material can be calculated readily (eqns (1)–(16)). Suitable analyses describing non-Fickian diffusion have not yet been developed. It is encouraging, therefore, that many composite materials seem to follow Fickian behaviour. Even in those cases when moisture transport is by a non-Fickian process the changes in moisture content with time can frequently be approximated using the Fick equations together with appropriate 'apparent' D and 'apparent' M_m values.

3.6 GLASS TRANSITION TEMPERATURE

The glass transition temperature T_g is an important parameter in the moisture transfer process. As was noted previously (Section 3.5) T_g marks the transition from a glassy to a rubbery state. In practice, the transition occurs over a temperature range. However, the glass transition temperature is a convenient parameter for identifying the condition at which significant changes occur in the molecular structure of the material.

The absorbed moisture may change (generally decrease) the glass transition temperature, thereby affecting the diffusion behaviour of the material. The Bueche-Kelley theory²⁰ provides the following estimate of T_g

$$T_g = \frac{\alpha_r(1 - v_f)T_{gr} + \alpha_f v_f T_{gf}}{\alpha_r(1 - v_f) + \alpha_f v_f} \quad (29)$$

where α is the expansion coefficient and v is the volume fraction. The subscripts r and f refer to the matrix (resin) and the fibre, respectively.

Equation (29) was developed for plasticized polymers. Although the data are limited, the existing data indicate that eqn. (27) gives the correct trend in T_g for epoxy resins as well as for fibre reinforced composites. The data also show that absorbed moisture may reduce the glass transition temperature by as much as 100°C (Fig. 3.6–3.8). Such a decrease in T_g due to moisture must be taken into account in the design of parts made of organic matrix composites.

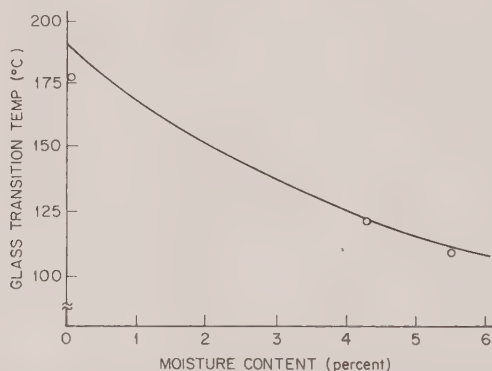


FIG. 3.6 Glass transition temperature versus moisture content for 3501-5 neat resin.²¹ Solid line is the result of Bueche-Kelley theory (eqn. 29).

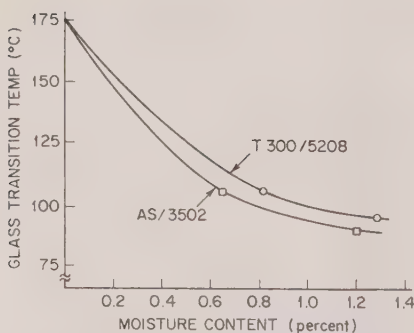


FIG. 3.7 Glass transition temperature versus moisture content for two types of graphite epoxy composite.²²

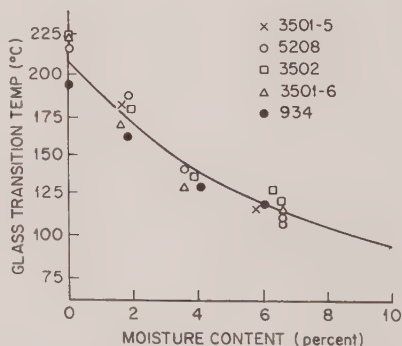


FIG. 3.8 Glass transition temperature versus moisture content for different neat resins.⁹

3.7 ENVIRONMENTAL CYCLES

The moisture transport characteristics of composites may change when the material is exposed to slowly changing environments for long time periods or if it is subjected to suddenly changing environments for short time periods. Most of the information available presently pertains to the effects of 'sudden', 'large' temperature changes, commonly referred to as 'thermal spikes'. Thermal spikes have generally been found to increase both the rate of moisture uptake and the rate of moisture loss. A plausible explanation of these phenomena is offered by photomicrographs taken of specimens subjected to thermal spikes. These photomicrographs often reveal microcracks, indicating that changes in the observed absorption-desorption patterns were caused by these cracks resulting from temperature-induced stresses.^{23,24}

The relationships between thermal spikes and material behaviour are not yet understood clearly. In fact, some of the evidence is contradictory. Significant changes have been observed in some materials subjected to thermal spikes,^{12,25} while only minor changes were found in some other materials under presumably similar spike conditions.^{8,26}

Slowly changing environments may also alter the material behaviour over long periods of exposure time. To gain an understanding of the effects of long term exposure, tests have been initiated in which samples are exposed to actual atmospheric conditions. The results of these tests are as yet limited. More data are expected to be forthcoming as these tests progress.

3.8 CONCLUDING REMARKS

The numerous studies made in recent years provide much of the needed information on the effects of the environment on fibre reinforced organic matrix composites. For many materials we now have analytical methods and data bases required in the design of practical engineering systems. There are still areas in need of further exploration. In particular, information is needed on problems where Fick's law is inapplicable, and on the effects of long term exposure and environmental cycles. Hopefully, the continuing efforts in these areas will soon provide analytical results and test data for these problems.

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Chapter 4

FATIGUE BEHAVIOUR OF FIBRE-RESIN COMPOSITES

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SUMMARY

The process of fatigue breakdown in fibre composites usually involves the progressive accumulation of matrix/interface cracking, with an associated loss in residual strength and modulus. This may continue until the residual strength is reduced to the cyclic stress, resulting in failure. However, tensile fatigue failure in many glass-dominated composites appears to be a fibre or strand property, independent of the matrix or interface. This is true both of cyclic and static fatigue, and the S-N properties also translate into resistance to crack initiation and propagation from notches in notch-sensitive cases. Exceptions to the fibre-dominated behaviour occur when a more severe fatigue mechanism operates, as with short fibres in very ductile matrices, or woven fabric reinforcement. This chapter reviews the general characteristics of the fatigue of composites with emphasis on recent developments in glass-fibre dominated behaviour.

4.1 INTRODUCTION

Fatigue resistance is a natural concern with fibre composites because their high specific properties make them attractive for mobile applications which often experience cyclic loading. In addition to their resulting significance, the fatigue-related properties of composites also provide a stimulating and challenging research area. This is due not only

to their construction from components of differing fatigue sensitivity, but also to the complexity of their damage states and eventual failure modes, which are unique composite features not inherent in the individual components.

Of the component materials of fibre reinforced plastics, the dominant reinforcement, E-glass, is known to suffer from a loss of strength with time under load due to a stress-corrosion mechanism common in inorganic glasses.^{1,2} The polymer matrices suffer from fatigue loading in several ways, including effects of time under load and load cycling, leading to a loss in stiffness and eventual failure, usually by fatigue crack growth.³ While independent data are not available for the fibre/matrix interface, its failure appears prominently in the development of fatigue damage in most composites. However, the challenge in the fatigue of composites lies not so much in the component materials as in the complexity of the modes of the damage which is often present over most of the lifetime, and the eventual failure mechanisms.^{4,5} In most cases there is a complex array of stable cracking which may initiate on the first fatigue cycle, and then change both quantitatively and qualitatively as the fatigue process progresses.⁶

Literature on the fatigue of composite materials has been accumulating at a rapid pace in the last ten to fifteen years, but there does not appear to be any completely comprehensive review available. Discussion which covers most topics of interest may be found in the limited reviews given in refs. 3 and 6-19. Of these, the most extensive lists of recent references are contained in the works by Hahn⁶ and Hertzberg and Manson.³

Like most of these efforts, this paper will not attempt a general review of the subject. Instead, the discussion will concentrate on the limited area of tensile fatigue of glass fibre composites, with emphasis on composites whose eventual failures are fibre dominated, rather than the result solely of transverse or interlaminar cracking. The topics covered, including damage development, failure mechanisms, lifetime characterization and macroscopic crack growth, are those in which the author has been directly involved. Before proceeding to these topics, a brief overview of the general subject will be presented.

4.2 TESTING CONSIDERATIONS

Details of test techniques will not be discussed in most cases since they are available in the cited references. In general, all tests use a sinusoidal

load-time function under load control. However, several points should be mentioned at the outset which are of sufficient importance to affect the choice of data selected for review, and which further confuse and confound an already complex subject. These are the effects of specimen internal heating at high test frequencies, strain rates in single-cycle tests when included with cyclic data, and test specimen geometry.

The most important problem is with internal heating of specimens at high frequency. This may result from the normal hysteresis in polymers,³ but in composites there may also be important frictional effects at stable cracks which develop during testing.^{6,21} Since polymer composites are generally poor thermal conductors, heat generated by cycling of the material tends to build up when the frequency is high, particularly at high stress levels where more heat is generated. Generally, this problem is most severe with glass fibre reinforcement because strain levels are greater than with higher-modulus fibres. Much of the early fatigue data were for glass reinforced materials, obtained on high speed machines at 30 Hz (cycles/s). Heating is often so severe under these conditions that a great deal of otherwise interesting data cannot be meaningfully interpreted. Such heating may have various complex effects which change with stress level,²⁰ becoming much less significant at low stresses; this effect could conceivably mimic the trends associated with fatigue limits. Heating effects may so dominate the fatigue behaviour at high frequencies that failure can be modelled as a thermal breakdown.²² In short-fibre reinforced thermoplastics such as nylon 66 it may be necessary to keep the frequency as low as 1 Hz to avoid significant heating.²³

This chapter is intended as a discussion of fatigue in the absence of any influence from internal heating. In practice, this requires testing at a sufficiently low frequency that specimen surface temperatures rise only a few degrees and then stabilize. This problem is pervasive in fatigue testing because of the practical importance that tests be run at as high a frequency as possible to study fatigue at long lifetimes. An attempt has been made in this paper to report only data which appear to be uninfluenced by internal heating, but in many cases the cited references contain some results which do not appear to meet this criterion. The reader is cautioned to consider fatigue data carefully in this respect, and this often requires tracing work back to the original source.

There are two additional problems related to frequency in interpreting S-N (cyclic stress v. log cycles to fail) curves. The first is the method of including the ultimate strength on such a plot. If the ultimate strength is

to have relevance to the cyclic results, it must be obtained at such a rate that the time to failure is consistent with a half-cycle of the fatigue test. In practice this is very important with glass reinforcement, due to the time sensitivity of the glass fibre strength, and ultimate strength results obtained at standard low displacement rates are usually significantly below those at fatigue rates. A related question is whether to plot the ultimate strength at one cycle or a fraction of a cycle, and investigators differ on this point. The same question would be relevant to cyclic tests if it were known exactly when the specimen failed; if failures occur at maximum load, then we should plot the data at the quarter- or half-cycle points, depending upon how the waveform initiated. In this chapter, the ultimate strength is plotted at one cycle, which tends to fall on the extrapolation of the cyclic data and also seems to be most reasonable to the author. Finally, there is the question of whether to run all of the tests for a given S-N curve at the same frequency or at the same load or strain rate, in which case the frequency should vary inversely with the maximum load. Since the maximum frequency chosen to avoid heating problems is limited by the relatively high stress tests, the use of a constant load rate allows higher frequencies at lower stresses (longer lifetimes), which is convenient. While our data have not shown any effect of these two approaches, Sims and Gladman²⁴ have presented data supporting the use of a constant load rate. In this review, a single frequency is given to indicate constant frequency S-N data, while a range of frequencies is given for constant load rate tests.

Fatigue results may also be affected by specimen geometry. In tension, the same problems with gripping, tabbing and dumbbell geometries are encountered as with static tests. Unidirectional glass and aramid composites tested in the longitudinal direction appear to present the greatest problems. Their high strength and strain to failure, coupled with low shear strength, make the use of straight-sided, tabbed specimens difficult due to tab delamination in fatigue, while dumbbell specimens tend to split at the shoulder. Promising results have been obtained with gradually tapering streamline specimens²⁵ and with specially wound, continuous fibre specimens.²⁶ Experience with multidirectional un-notched glass fibre composites indicates that dumbbell specimens may give gauge-section failures if the specimen geometry is tailored to the specific material and fibre orientation.²⁷⁻²⁹ While this chapter deals primarily with tensile fatigue, it should be noted that test specimen geometry and buckling constraint pose significant problems for tests which include compressive loads.^{30,31}

The result of an improper specimen geometry would be the measurement of an apparently lower strength due to failure caused by a stress concentration. However, it will be shown later that fatigue loading may reduce the effect of a stress concentration, resulting in an S-N curve with a lower strength at low cycles, but a more nearly correct trend at higher cycles. In this context a stress concentration may result from anything from a notch⁵ to grip complications.²⁵ While such effects may not always be eliminated, they should at least be minimized by specimen design.^{5,25,28}

4.3 GENERAL TRENDS OF FATIGUE RESISTANCE AND DAMAGE ACCUMULATION

4.3.1 Introduction

This section is intended to provide a brief overview of fatigue resistance and damage accumulation in relatively long-fibre composites; very short-fibre composites ($l/d < 100$) may be distinctly different, and will be discussed later. Only the effects of cyclic loading on tensile coupons of various composites will be considered, as later sections will cover the effects of loading conditions and notched specimens. The loading conditions are defined by the stress ratio, R , as

$$R = \text{minimum stress/maximum stress} \quad (1)$$

4.3.2 Fatigue Resistance of Various Composites

The greatest effect of fibre properties is observed in the longitudinal fatigue of unidirectional materials. Figure 4.1 illustrates the variation from almost complete insensitivity to fatigue for the Type I, high modulus graphite composite^{6,12} to the loss of approximately 10% of the static strength per decade for E-glass.^{29,32} Type II graphite⁶ and Boron⁶ fall slightly below Type I graphite, and aramid falls between these two and E-glass.²⁵ The curves in Fig. 4.1 are approximate trend lines for the results given in the references. The relative performance shown in Fig. 4.1 is approximately in order of modulus and strain at failure, with the stiffer materials which are cycled at lower strains showing greater fatigue resistance.

Figure 4.2 indicates the effects of testing boron/epoxy in transverse

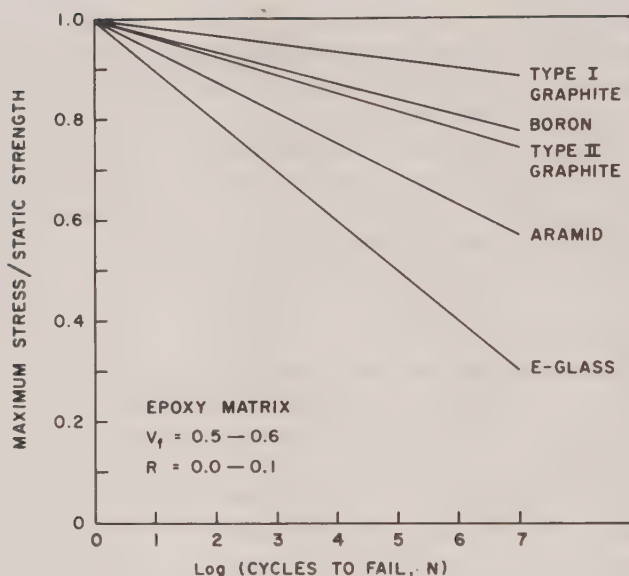


FIG. 4.1 Trends of longitudinal tensile fatigue S-N data for unidirectional composites with various fibres (from refs. 6, 12, 25, 29 and 32).

tension (fibres perpendicular to the load) and in-plane and interlaminar shear.^{6,33} The shear results are similar to those reported for glass and graphite composites.^{12,33} The trend lines in Fig. 4.2 correctly imply that multidirectional composites which have good fatigue resistance in the longitudinal plies are likely to develop cracks in the off-axis plies. In fact, most multiaxial composites develop damage in the plies or strands oriented in an off-axis direction, frequently on the first loading cycle.

4.3.3 Damage Development

Figure 4.3 shows trend lines for failure and for the initiation of transverse debonding and cracking in two glass composites, randomly oriented chopped strand mat (CSM) reinforced polyester³⁴ and 0°/90° crossplied glass/epoxy²⁷ (for the laminate constructions given, 0° will refer to the applied stress direction). Debonding and cracking develop in both materials on the first fatigue cycle over most of the stress range. At stresses less than that at which damage develops on the first cycle, damage initiation is observed after some period of cycling, and an S-N curve may be

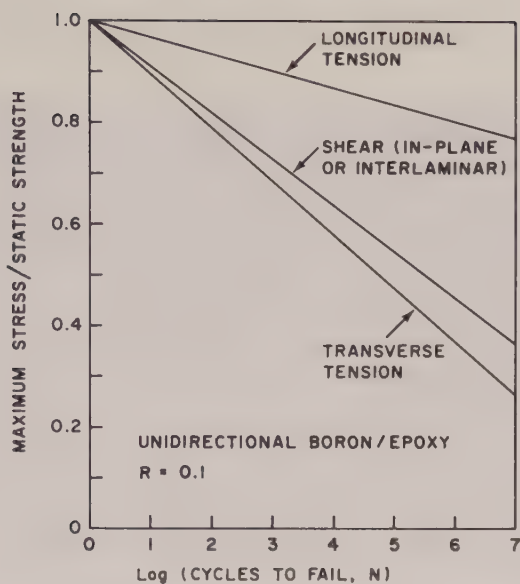


FIG. 4.2 Trends of S-N data for unidirectional boron/epoxy tested in various directions (from Refs. 6 and 33).

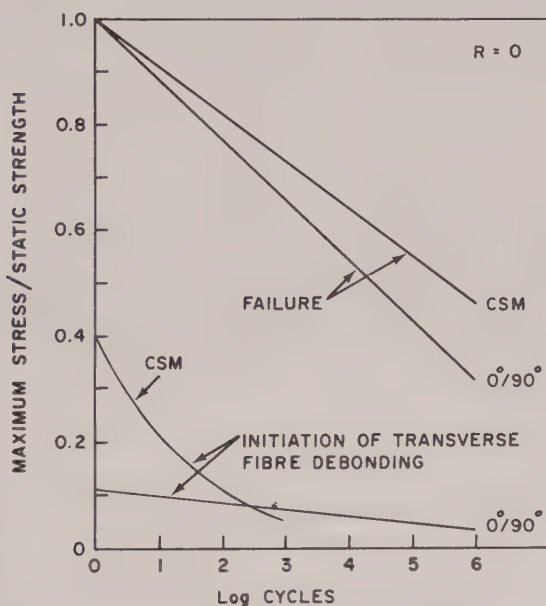


FIG. 4.3 Trends of cycles to initial damage development and final failure for CSM glass/polyester (from ref. 34) and $0^\circ/90^\circ$ glass/epoxy (from ref. 27).

represented for damage initiation similar to that for failure. After 10^6 cycles, damage is observed in glass fibre systems even at stresses less than five per cent of the static strength.^{27,34}

The nature of transverse debonding and cracking is illustrated in Figs. 4.4–4.6 for R50 SMC material. R50 SMC is a composite containing 50% by weight chopped glass strand, polyester resin and calcium carbonate filler.^{29,37} Figure 4.4 shows the pattern of cracks, which clearly run parallel to the local fibre direction where possible. The cracks usually terminate or deflect when they encounter fibres crossing their path; however, a few stray fibres in an otherwise matrix-rich region may be broken, as in Fig. 4.5, particularly after many fatigue cycles. Figure 4.6 shows a cross-sectional view of a crack in a strand which is typical of cracks in almost all of the composites discussed here; the cracks propagate along the fibres, in the interface wherever possible, occasionally breaking through the small regions of matrix between fibres as necessary. One exception to this characteristic is in aramid fibre composites, where some cracks have been shown to split the fibres axially.²⁵ (Kim and Ebert³⁶ report gross splitting and cracking of the fibres in a glass fibre system at an early stage in the lifetime, but our efforts to reproduce these results have been unsuccessful.) Two other common types of damage are delaminations between plies, which differ only slightly from Fig. 4.6 but often form at free edges,³⁸ and cracks in matrix-rich regions. The latter, called matrix cracks,¹¹ are common in chopped strand materials with good strand integrity (fibres remain tightly grouped in the strand). Matrix cracks tend to form normal to the applied tensile stress at stress levels higher than interface-related cracks.²⁷ In many cases, transverse cracks and matrix cracks in CSM materials, or transverse and delamination cracks in laminates, appear to form an interconnected network. In unidirectional ply laminates with high fibre content, such as the $0^\circ/90^\circ$ material in Fig. 4.3, the transverse cracks form predominantly in the plies most nearly normal to the load, and occur at a regular, close spacing even in single cycle tests.^{27,35}

Figure 4.7 shows the trend of transverse crack accumulation in several composites. The crack density on this plot is normalized by the crack density either at failure or at the number of cycles closest to failure where data were available in the reference. The cycle ratio is the number of cycles endured, n , divided by the number of cycles to failure, N ; the ratio is plotted on a linear scale rather than the log scale of typical S–N curves. In each case the crack density increases rapidly at the beginning,

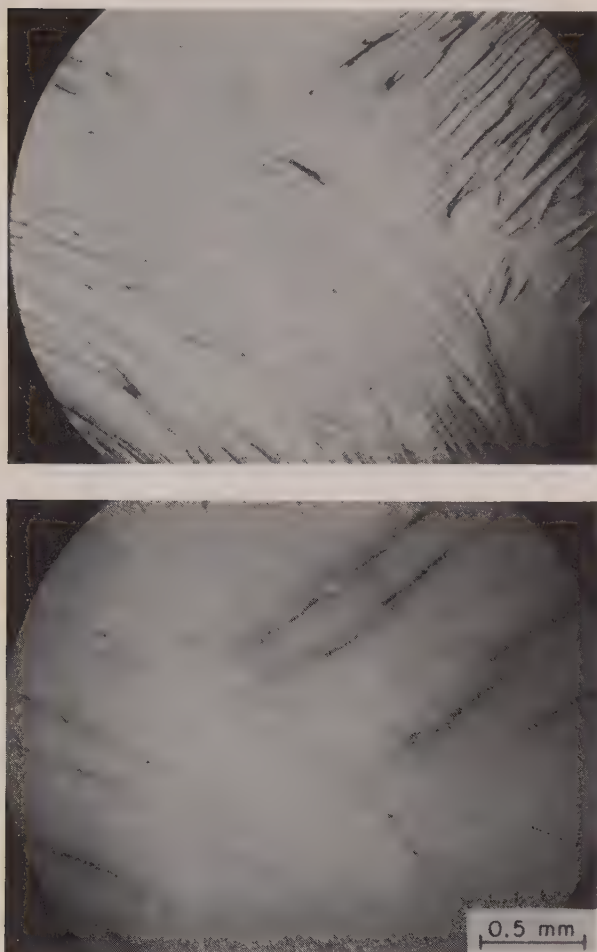


FIG. 4.4 Polished, stained surface of SMC-R50 specimen which failed in fatigue at 2.3×10^6 cycles; top shows arrangement of strands on surface, bottom shows crack pattern revealed by stain in cross-polarized light at the same position.

followed by a gradual, less rapid increase over most of the lifetime, with an increased rate just prior to failure in some cases. As indicated in Fig. 4.3, transverse cracking is already present after the first cycle over most of the stress range for glass composites, which operate at higher strain levels than do graphite composites.

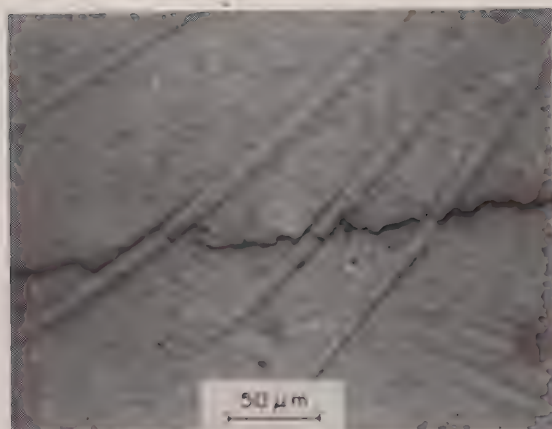


FIG. 4.5 Matrix crack breaking dispersed fibres in specimen from fig. 4.4

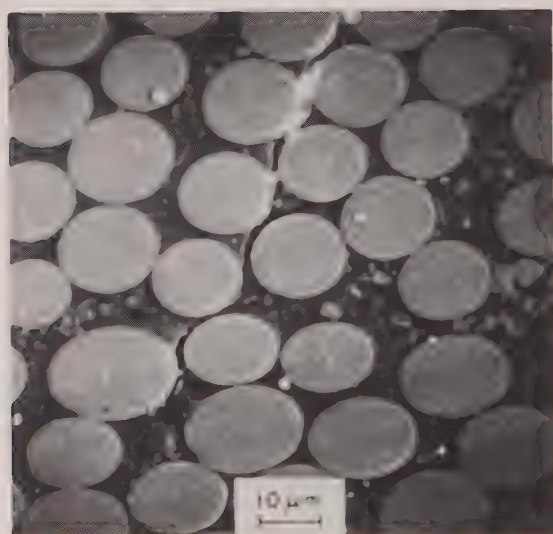


FIG. 4.6 Transverse crack in strand on polished cross-section of specimen from fig. 4.4.

The crack spacing in graphite/epoxy laminates has been found to reach a particular value at failure, dependent on the ply arrangement but independent of load history; this cracked condition has been termed the 'characteristic damage state' by Reifsnider.⁸ Recent unpublished data on

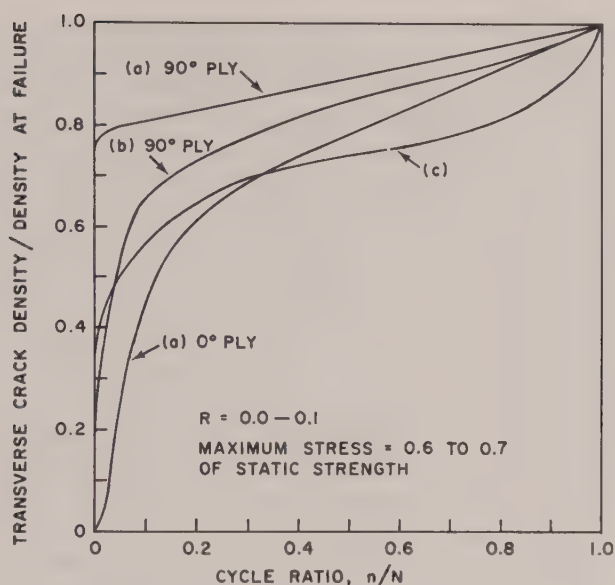


FIG. 4.7 Trends of stable damage accumulation for (a) $[0^\circ/90^\circ]$ Glass/Epoxy (from Ref. 35), (b) $[0^\circ/90^\circ/\pm 45^\circ]$, Type II Graphite/Epoxy (from Ref. 8) and, (c) CSM Glass/Polyester, Transverse fibre debonding (from Ref. 4).

several SMC compositions support this view. Contrary to our finding, Howe and Owen⁴ report that the matrix crack density at failure is greater for fatigue at lower stresses, and is greater in fatigue than in static tests for CSM glass/polyester. Another exception appears to be laminates such as $[0^\circ/\pm 45^\circ]$, graphite/epoxy, where the 0° plies fail before the 45° plies in a static test, but the greater fatigue sensitivity of the 45° plies results in their cracking prior to 0° ply failure in fatigue.⁶

4.3.4 Residual Properties and Failure Modes

Howe and Owen⁴ have found that the normalized damage accumulation curve for CSM glass/polyester given in Fig. 4.7 is a stress-independent master curve for damage accumulation at several stress levels and R values; a similar master curve is reported in the same study for matrix crack accumulation. They also report that the residual static fatigue curve (constant stress v. log time to fail) is shifted to lower stresses as the n/N ratio increases; the residual strength is found to be a function only of n/N for various stress levels and R values. This close association between damage accumulation and residual strength (as well as modulus) has also

been reported for $0^\circ/90^\circ$ glass/epoxy by Broutman and Sahu,³⁹ but they find that the residual strength is stress dependent as well as cycle ratio dependent. Owen *et al.*^{4,40} attribute the decrease in residual strength in CSM glass/polyester to a sequence of transverse fibre debonding serving as initiation sites for matrix cracking, which in turn leads to delamination of strands in the load direction. Broutman and Sahu³⁵ similarly associate the reduction in residual strength of $0^\circ/90^\circ$ glass/epoxy with the progression of transverse cracks from the 90° ply into the ply interface and also into the 0° plies. Hahn⁶ has also shown that stress levels in the transverse direction of the 0° plies resulting from constraint on Poisson's ratio contraction by the 90° plies may be sufficient to generate transverse cracks in the 0° plies in fatigue.

The process of damage accumulation and the associated loss in residual strength and modulus appear to be qualitatively well understood. The loss in residual properties appears consistent with the damage sustained, the damage being the result of cracks in the matrix and fibre/matrix interface. While fatigue data are scarce for the matrix and interface independently, polymers and adhesive bonds are known to degrade in fatigue and to suffer crack growth under cyclic loading.³ However, the rational picture of progressive degradation related to matrix and interface cracking is not easily extended to anticipate final failure, particularly in cases dominated by the fibres. If a specimen is cycled at a moderate stress such as 50% of the static strength, the progressive loss in residual strength with cycles is difficult to trace to a point where the residual strength approaches the maximum cyclic stress, and failure might reasonably occur. Usually the residual stress remaining as the mean lifetime is approached is still much greater than the cyclic stress.^{4,5,41} Failure appears to involve some localized mechanism resulting in fibre fracture; some evidence of such fibre failure just prior to complete specimen failure has been reported.^{4,8} In woven glass fabric reinforced polyester, final failure at stresses above 30–40% of the static strength appears to be associated with separation of the material at the weave crossover points, which may suddenly increase the local fibre stress or result in friction and wear of the material at this point.⁴² The extensive residual strength data reported for $0^\circ/90^\circ$ glass epoxy by Broutman and Sahu³⁵ differ from most other data in that the residual strength does approach the cyclic stress prior to failure. It is difficult to judge the significance of this difference because the residual strength results appear to have been obtained at a strain rate orders of magnitude lower than that in the cyclic tests; and the residual strength at the proper rate may in fact have been much greater than the cyclic stress.

Few efforts to predict the S-N curve of composites have been reported. One approach which has shown promise is the prediction of the S-N curve of multiaxial composites based on the S-N curves of fibre- and matrix-dominated unidirectional cases. It is found that the same failure criteria useful in predicting the static strength of laminates may be applied to predict the strength at a given number of fatigue cycles for similar cases.^{6,43-45} These criteria are approximate, assuming linear behaviour, which is a simplification even in the static case and less representative of the changing mechanical properties in fatigue. However, this approach is supported by the observation that gross failure modes in fatigue are generally similar to the static modes;^{5,6} on a microscopic scale Howe and Owen⁴ report a difference in crack characteristics, as a much greater amount of powdered material occurs inside the transverse cracks of glass composites in fatigue. In boron/epoxy laminates with enough 0° plies to dominate the behaviour, the ratio of laminate strength to longitudinal ply strength was found to be approximately the same for static strength and fatigue strength at 10^6 cycles.^{4,6} These results suggest that the failure of some composites may be no more complex in fatigue than in static loading, despite the accumulation of damage and gradual loss in residual properties; those composites which are fibre dominated in static tests may often remain so in fatigue despite the tendency of the matrix and interface to break down.

There are clearly many statistical problems of importance in the fatigue of composites. While these are primarily of importance in design, they could also relate to a basic understanding of the fatigue resistance in some cases. No attempt will be made to review this area in this paper, and the results reproduced here have not been treated statistically. Discussion of statistics as they relate to fatigue may be found in review articles (refs. 3 and 6).

4.4 TENSILE FATIGUE OF GLASS FIBRE DOMINATED COMPOSITES

4.4.1 S-N Data for Typical Composites

The relative insensitivity of graphite and boron composites to fatigue loading along the fibre direction is evident in Fig. 4.1. The much greater sensitivity to loading in shear or transverse tension (Fig. 4.2) results in a strong influence of the matrix/interface dominated properties on laminates with a predominance of off-axis plies, such as

$[0^\circ/\pm 45^\circ/90^\circ]$.^{6,46,47} Although glass fibre composites operate at higher strain levels and tend to develop transverse cracking earlier, it is also true that the fatigue resistance in the longitudinal direction (Fig. 4.1) is similar to that in transverse tension and shear (Fig. 4.2). The result of this is, that an unexpectedly broad range of glass fibre composites behave in a fibre-dominated manner, with their normalized composite fatigue sensitivity similar to that in Fig. 4.1 for the unidirectional material tested along the fibre direction.

Figure 4.8 shows S-N data for three very different fibre composites: $0^\circ/90^\circ$ unidirectional ply glass/epoxy, injection moulded glass/polycarbonate, and SMC. The reinforcement in these three materials is, respectively: continuous fibre ($V_f = 0.5$), very short, partially oriented fibre

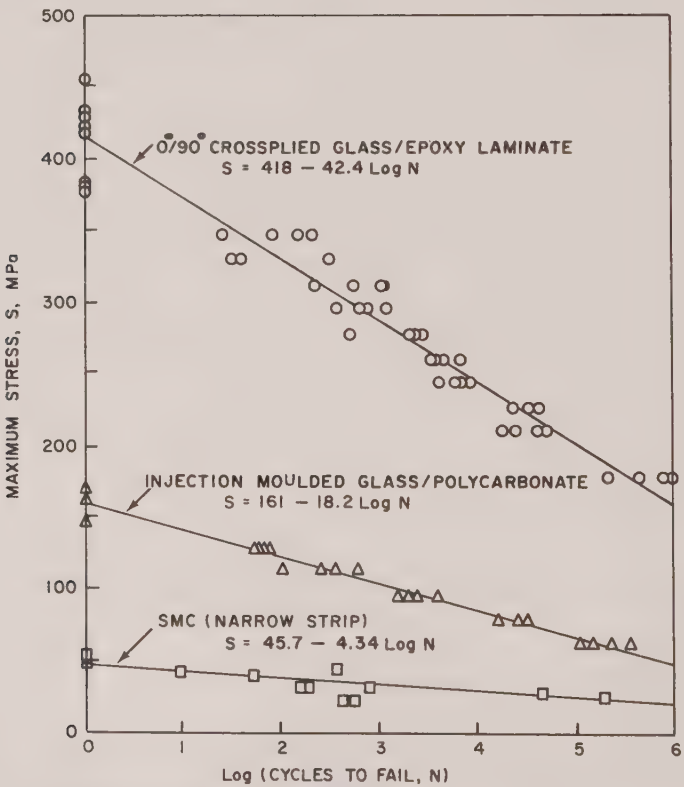


FIG. 4.8 Typical tensile S-N data for glass fibre composites (top to bottom: materials no. 4, 6 and 11 in table 4.1), $R=0.1$ (from ref. 29).

(less than 1 mm length) ($V_f = 0.24$), and chopped 5-cm long randomly oriented strand ($V_f = 0.15$). The SMC was tested in a long, narrow (25×0.64 cm) strip to obtain the weakest, most matrix-sensitive properties,²⁹ and would normally have approximately twice this static strength. In each case the S-N curve plotted on a semi-log scale is in good agreement with the linear least-squares curve fit. The linear fits give S-N curves of the form

$$S = \text{UTS} - B \log N \quad (2)$$

where S is the maximum stress during each cycle, UTS is the single cycle intercept of the linear fit (lying close to the average ultimate tensile strength obtained at the appropriate load rate and plotted at one cycle), B is the slope of the line in units of stress per decade of cycles and N is the cycles to complete failure. The ratio UTS/B is a normalized measure of the steepness of the S-N curve (its inverse, B/UTS , is the fractional loss in tensile strength per decade of cycles, perhaps a more meaningful parameter). The UTS/B ratios of the three materials in Fig. 4.8 in order of descending strength are 9.8, 8.8 and 10.5, all close to 10, or 1/10 of the strength per decade.

As noted earlier, the literature on the fatigue of glass fibre composites is replete with uncertainties from specimen heating, test rate and specimen geometry effects. However, a variety of materials representative of most of the useful glass fibre reinforced plastics have been tested under conditions which appear not to involve any major discrepancies. The materials listed in Table 4.1 all have S-N curves in tension ($R = 0.0-0.1$) which appear similar to Fig. 4.8 (some exceptions are discussed later). The data for each have been fitted to a linear relationship, and the results are summarized in Fig. 4.9 as a plot of the UTS v. the slope of the S-N curve, B . The rate of strength loss of all of these composites is surprisingly invariant; neither matrix, interface, void content, filler content, fibre content, dispersion nor length make much difference. In fact, the highest strength case plotted is for glass strand with no matrix (or interface) present. These results are interpreted as clear evidence that tensile fatigue up to 10^6 or 10^7 cycles in the materials listed in Table 4.1 is not only a fibre dominated property, but is a property which derives entirely from the fibres or strands.

4.4.2 Origin of S-N Behaviour

The strand results have only recently been obtained, and may be found in more detail in ref. 29. The test method used a 20 cm long gauge section and combined rubber and epoxy bonding in the tabs to ensure gauge

TABLE 4.1
MATERIALS IN FIG. 4.9 (ALL E-GLASS FIBRES)

No.	Reference	Description	Matrix	Nominal fibre volume fraction
1	26	Unidirectional	Epoxy	·50
2	26	Unidirectional	Epoxy	·33
3	26	Unidirectional	Epoxy	·16
4	28	0°/90°	Epoxy	·50
5	23	Injection moulded	Nylon 66	·23
6	23	Injection moulded	Polycarbonate	·24
7	23	Injection moulded	Polyphenylene sulphide	·25
8	23	Injection moulded	Poly (amide- imide)	·19
9	42	Chopped strand mat	Polyester	·29
10	29	SMC (64 × 64 × 32 cm)	Filled polyester	·15
11	29	SMC (25 × 64 × 32 cm)	Filled polyester	·15
12	29	SMC-R50	Filled polyester	·35
13	21	[0°/±45°/90°] _s	Epoxy	·50
14	4	Chopped strand mat	Polyester	·20
15	29	Impregnated strand	Polyester	·23
16	29	Impregnated strand	Epoxy	·45
17	29	Impregnated strand	Toughened epoxy	·49
18	29	Unimpregnated strand	None	1·00

section failures. This was of particular importance for the unimpregnated strands, to avoid possible ambiguity if failures were initiated in the tab adhesive where the ends of the strands were effectively impregnated. Table 4.2 gives the S-N curve parameters for various strand tests using ECG 135 strand with 1·4% by weight chrome silane binder (PPG) except as noted. The ratio UTS/V_f is the effective fibre strength ignoring any matrix. The matrix impregnation increases the fibre UTS as expected, but the rate of fatigue degradation, UTS/B , is not significantly changed by the presence of the matrix. Unimpregnated strands cleaned in acetone to remove the binder/coupling agent showed the same UTS/B ratio, and unimpregnated strands tested in a silicone oil bath gave similar results.

Unimpregnated strand data have also been obtained under other tensile fatigue conditions, ranging from $R=0\cdot1$ to constant load, static fatigue ($R=1\cdot0$). Figure 4.10 gives the UTS/B ratio plotted against the R value for the unimpregnated strands, epoxy impregnated strands and

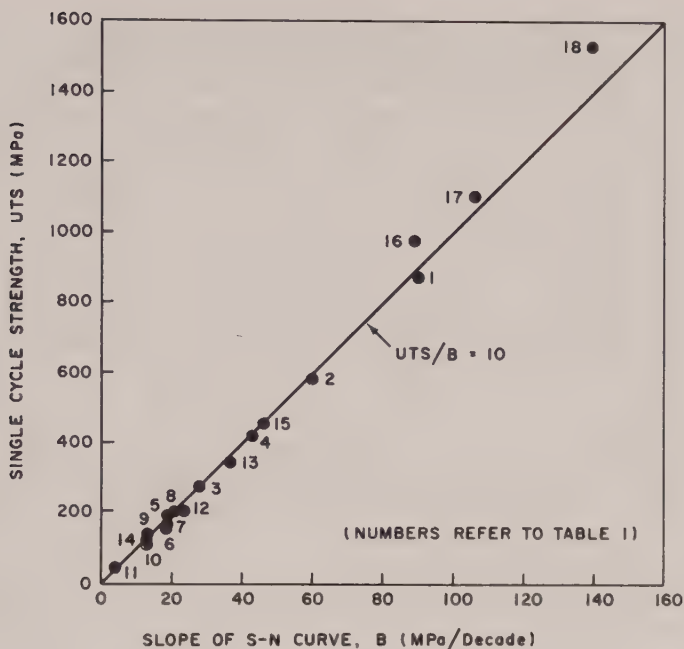


FIG. 4.9 Single-cycle tensile strength v. slope of S-N curve for materials listed in table 4.1, $R=0.0-0.1$ (from ref. 29).

TABLE 4.2
S-N CURVE PARAMETERS FOR STRAND TESTS (FROM REF. 29)^a

Matrix	V_f	UTS (MPa)	UTS/ V_f (MPa)	UTS/B
Unimpregnated	1.0	1530	1530	11.0
Unimpregnated (Cleaned strands)	1.0	1219	1219	11.0
Polyester	.23	455	1980	10.0
Epoxy	.45	971	2160	11.0
Rubber-modified epoxy	.49	1102	2250	10.4
Unimpregnated ^b	1.0	1426	1426	11.6

^a $R=0.10$, 5 Hz.

^b Initial tests on strand removed from woven roving, 5-10 Hz.

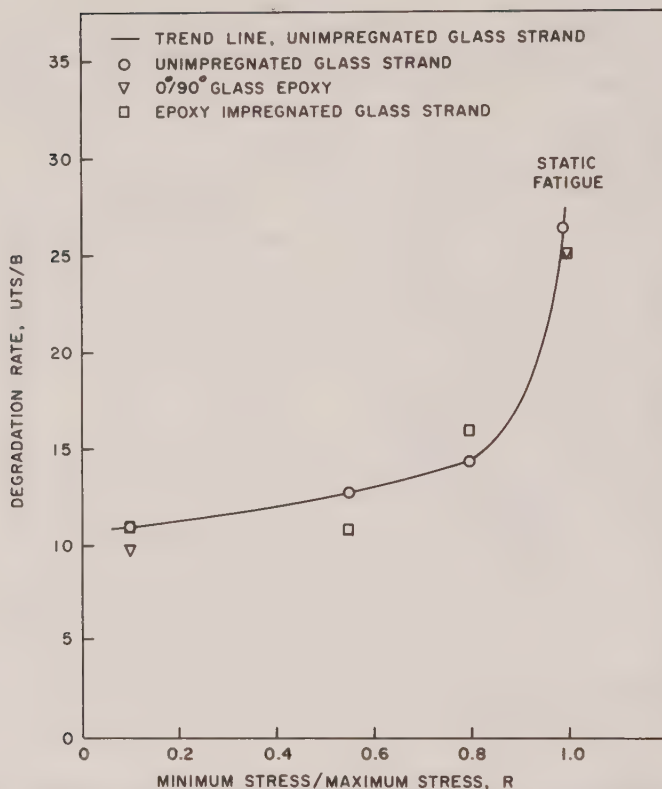


FIG. 4.10 Degradation rate v. stress ratio for composites and unimpregnated strand, 5 Hz (from ref. 29).

0°/90° glass/epoxy laminates.²⁹ The results show that the degradation rate of the unimpregnated strands is the same as for composites over the entire range of tensile loading. Both show a much more rapid strength loss in cyclic loading than in static fatigue. Thus, it is concluded that tensile fatigue in general is a fibre or strand property, independent of matrix or interface.

A somewhat similar normalization of S-N data for more limited groups of materials has shown very similar curves when the data are plotted as a function of strain, by dividing the stress by the composite modulus.^{14,32}

The origin of the cyclic fatigue effect in the glass strands has not been established, but several possibilities are apparent. The slope of the

stress-log time curve in static fatigue is thought to be a result of stress corrosion cracking of the glass material, present in bulk glass or in a single fibre, generally giving a loss of 3–5% of the short term strength per decade of time under ambient conditions.^{1,2,48} This approximate static fatigue rate has been observed in various glass fibre dominated composites.^{29,48 50} The strong cyclic effect shown in Fig. 4.10 is not expected for bulk inorganic glasses, which generally show a similar degradation rate whether under cyclic or constant load.^{51,52} The difficulty with existing data on inorganic glasses is that the materials reported have static UTS/ B ratios close to the value of 10 observed in Fig. 4.10 under cyclic loading, so any difference between cyclic and static fatigue may be undetectable. This is also the case with tests of a composite of soda-lime glass sheets alternated with ductile polyethylene layers, where no cyclic effect was reported.⁵³ One study which compared cyclic and static fatigue of silica fibres found an intermediate degradation rate, with some shift to shorter lifetimes with cyclic loading, but little change in UTS/ B ratio.⁵⁴

If the cyclic effect is not present in single E-glass fibres, then it must result from fibre-fibre interaction. In the unloaded composite there is almost always a predominance of fibre-fibre contact as evident in the micrograph of an *in situ* strand in Fig. 4.6. Even with the matrix intact, it is not difficult to envisage high contact stresses between fibres, perhaps including some relative movement and attendant wear if there is any fibre misalignment. Since matrix and interface cracking is present to some extent in all of the composites in Table 4.1 prior to failure, the process could also be one of a breakdown in the protective role of the matrix, leading to performance similar to groups of fibres without matrix. Thus, it is not clear whether matrix/interface damage development plays a direct role in cyclic fatigue failure. In terms of materials development, it would clearly be beneficial to establish whether the cyclic effect is inherent in a single fibre, as in the static fatigue effect, or whether it is a result of contact between fibres. Unambiguous single fibre data would clarify this point.

The model for the S-N fatigue behaviour of glass composites which derives from this work is one of the local groups of fibres responding as they would in the unimpregnated strand. For this simple model to control the behaviour of a typical composite, the following appear to be necessary:

1. The single cycle UTS of the composite must be reached when some

dominant strands, plies or fibre agglomerations reach their local strength, fail and lead directly to failure of the composite.

2. In fatigue, corresponding dominant fibre regions fail due to the mechanism operating in the unimpregnated strands, and the composite fails when these fibres fail.

This would lead to linear S-N curves including the static strength, with the same UTS/B ratio as shown by the unimpregnated strands. Differences in matrix, interface and reinforcement style would alter the UTS, but not the relative fatigue performance. The UTS in unidirectional material tested along the fibres is a relatively simple property controlled by the fibre strength and V_f ; in random, discontinuous fibre systems these parameters are also important, but UTS prediction is more complex.⁹

It is not obvious that a typical composite test specimen, with a complex array of stable damage and dimensions much greater than a single strand, would follow this simple formula. However, static and fatigue failure modes are generally similar in appearance, and in all cases investigated do involve fibre failure, including the very short fibre injection moulded materials.^{23,55} Some composites which do not follow this model have been demonstrated,²⁹ and others can be hypothesized.

4.4.3 Non-typical S-N Behaviour

Taking the S-N curves in Fig. 4.8 and the 10% loss in UTS per decade in Fig. 4.9 as typical behaviour for glass fibre dominated composites, some non-typical cases can be identified. Perhaps the most limiting of these pertains to size effects for large specimens or applications. Under monotonic loading, failure of a significant region of fibres in a fibre dominated composite may lead to immediate total failure of the specimen. However, at low cyclic loads such a region may fail without leading to catastrophic specimen failure, but requiring the subsequent failure of other regions to form a large enough flaw to reach a critical condition at the maximum cyclic stress, depending on the notch sensitivity of the composite. This can be clearly demonstrated for notched specimens, as will be shown later. Size effects which may also relate to this explanation have been demonstrated for SMC materials.²⁹ Narrow regions of SMC, whether long and weak or short and relatively strong, were found to lose approximately 10% of their UTS per decade (Fig. 4.9). Wider specimens showed linear S-N curves, but the UTS/B ratios were significantly different from 10 — either higher or lower, depending upon the formulation. Weaker materials tended to have less steep S-N curves than

expected, stronger materials more steep. These specimens varied significantly in strength from region to region, and developed large stable cracks in fatigue prior to failure. Thus, the fundamental fatigue response described in the preceding sections applies only to regions of composite of limited size; failure of large specimens or structures may require consideration of the development and progression of zones of local failure.

Another type of non-typical behaviour results from the influence of a more severe mechanism of degradation than that exhibited by the fibres. An illustration of this is the case of $[0^\circ, \pm 45^\circ]$ graphite/epoxy described by Hahn.⁶ Under static loading the 0° ply fails before the 45° plies; however, because the matrix-dominated 45° plies are more sensitive to fatigue, they fail first in cyclic tests, leading to a greater fatigue degradation rate than if the failure were controlled by the 0° plies. With glass reinforcement the fibres degrade at a much faster rate than the 0° graphite/epoxy ply, so the example cited is unlikely to occur with glass composites even if the static behaviour were similar. An analogous effect is found with glass composites if the reinforcement is woven, as shown in Fig. 4.11. The woven fabric material has an initially steep S-N curve which results from failure rapidly following delamination at the weave cross-over points.⁴² The high-stress part of the S-N curve has a UTS/ B ratio of approximately six for several woven fabrics with a polyester matrix. This mechanism does not operate at lower stresses, and the S-N curve flattens dramatically, approaching the expected lifetime for UTS/ $B=10$. The extensive early work reported by Boller^{56,57} appears to indicate that such curves have a less steep initial slope with epoxy matrices but retain a similar general shape. This would be consistent with the greater interlaminar strength expected for epoxies, but the data may also have been affected by temperature build up. The reason that the weave separation leads to rapid failure is not clear, but may be due to either extreme wear from movement at these points⁴² or an increase in the stress in the strands after separation, since they may then tend to straighten.

Mechanisms having effects analogous to those in woven fabrics are not difficult to envisage. A similar one has been shown in wet environments for static fatigue of impregnated strands of several fibres and matrices.⁴⁸ In this case the strengthening effect of the matrix on the strand may be broken down by moisture attack on the interface, and the strength may revert to that of the unimpregnated strand. The potential difference in strength is evident in Table 4.2. Such an effect results in a steep static or

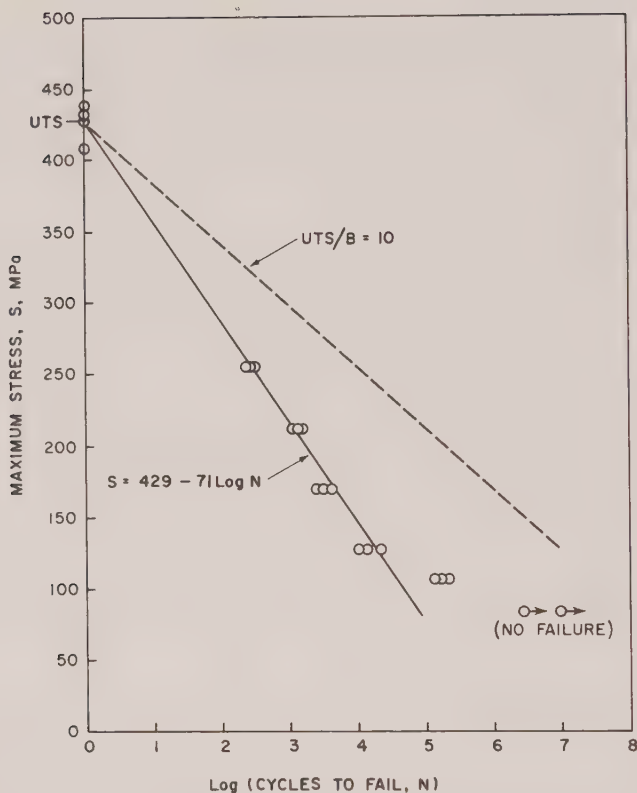


FIG. 4.11 S-N curve for style 181 woven fabric reinforced polyester compared with non-woven curve, $R=0.1$ (from ref. 29).

cyclic fatigue curve which may shift to the unimpregnated curve after debonding has occurred, and thus appear to flatten at low stresses.

Non-typical behaviour might be expected for short-fibre composites, with changes from fibre to matrix domination as the fibres become less effective due to debonding or yielding around their ends. Surprisingly, such an effect was not observed for the injection moulded thermoplastics included in Figs. 4.8 and 4.9. Although cracks tend to move in a fibre-avoidance mode for materials with moderate fibre contents and fibres generally less than 1 mm in length,^{23,55} many fibres are still observed to be broken by cracks if the reinforcement is glass. Graphite fibres in similar systems are not broken, and the fatigue response is much more

sensitive to the matrix. Figures 4.12 and 4.13 compare the S-N curve fits of different matrices with glass and graphite (carbon) reinforcement. The glass systems all lose approximately 10% of their strength per decade, while the graphite systems vary, showing better fatigue performance (but lower strength) with the brittle polyphenylene sulphide matrix, and steeper curves for the ductile matrices.

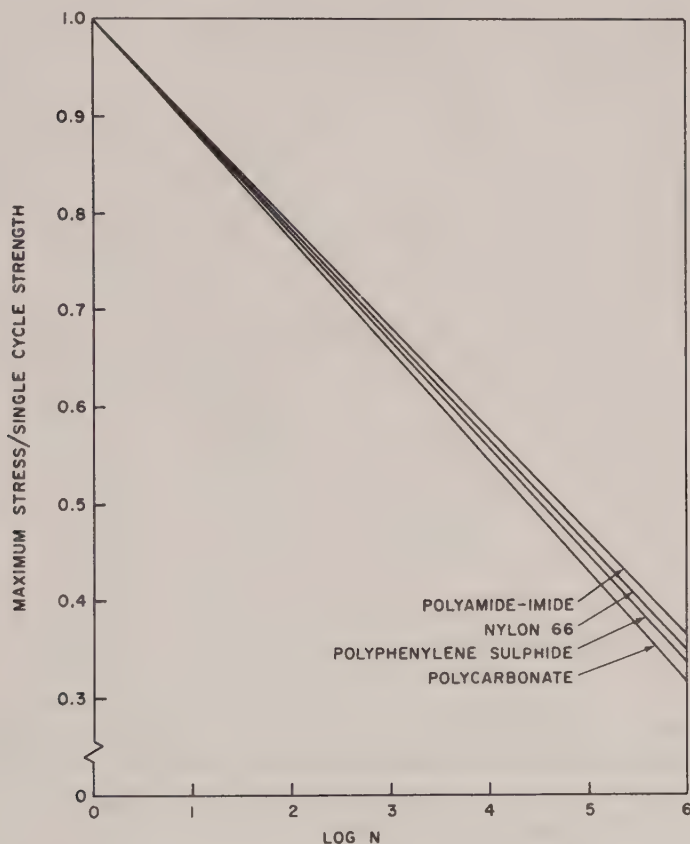


FIG. 4.12 Normalized tension-tension S-N fatigue curves for glass-reinforced thermoplastics (from ref. 23).

The S-N data for the glass/nylon 66 system in Fig. 4.12 was not well represented by the linear curve fit.^{2,3} It showed a slight non-linearity, being steeper at high stress, and also showed a more ductile stress-strain curve, with some evidence of local yielding. When tested at -30°C the

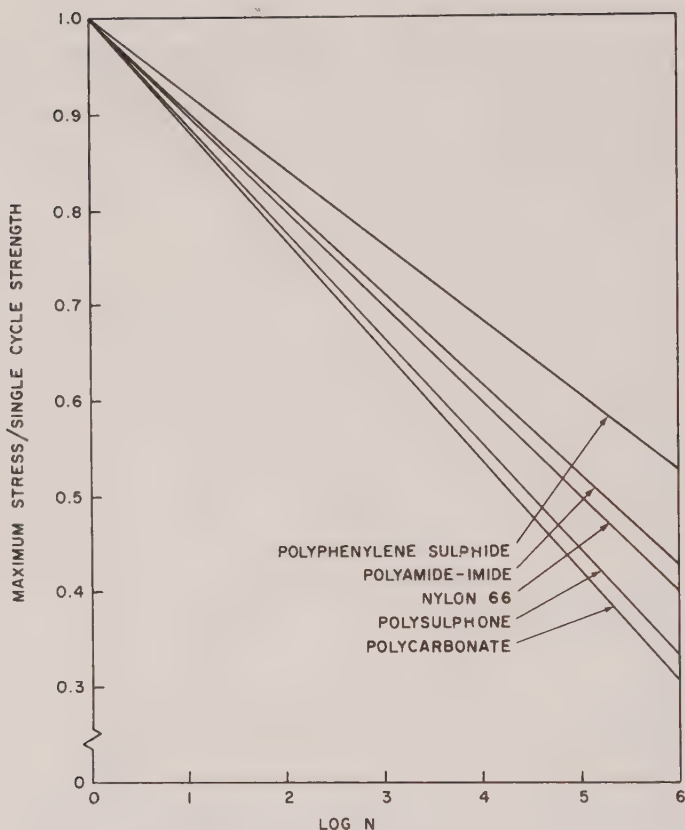


FIG. 4.13 Normalized tension-tension S-N fatigue curves for carbon-reinforced thermoplastics (from ref. 23).

nylon 66 matrix is less ductile, and the composite returned to the expected linear S-N curve (unpublished data). Thus, a very ductile matrix may result in a non-linear S-N curve with short fibres, and this may be more prominent at low fibre contents.

A last effect which will be demonstrated in the next section on notched specimens relates to the blunting of flaws in fatigue. Simply stated, a flaw or notch, which may lead to fracture at a low applied stress in a notch sensitive material, may be effectively blunted by the development of an enlarged stable matrix/interface cracking zone in fatigue. This can result in an initially flat S-N curve as the stress concentration at the flaw is reduced, followed by a normal degradation rate after that.

4.5 NOTCH EFFECTS AND FATIGUE CRACK GROWTH

4.5.1 Notch Effects

The combination of sharp notches and cyclic loading has unexpected results with fibre composites as compared with other materials. With most metals⁵⁸ and polymers,³ the cyclic loading of a sharply notched specimen results in the extension of a very sharp crack from the notch. The crack grows in a stable fashion until it reaches a critical length for fracture. Cracks grown under cyclic loading in such materials are usually sharper than those in monotonic tests, since their crack-tip yield zone is decreased in size approximately with the square of the stress intensity factor, K_I ; fatigue crack growth typically involves K_I values much lower than the monotonic fracture toughness, K_{IC} . This response is generally reversed for fibre composites. The analogous 'yield' zone in composites is, in fact, a damage zone consisting primarily of matrix/interface cracks growing parallel to the fibres and ply interfaces.^{5,59} In effect, the damage zone blunts a sharp crack and reduces the elastic stress concentration which would otherwise exist. In fatigue, this damage zone may grow larger, thus further blunting the notch and reducing the stress concentration.⁵

Figure 4.14 gives S-N data of 0°/90° glass/epoxy tensile specimens with and without sharp notches⁵ (the dashed lines are approximate upper and lower bound trend lines for each group of data). The unnotched S-N curve is the same as that given in Fig. 4.8, with a UTS/ B ratio close to 10. Specimens 7.6 cm wide with 1.5 cm long double-edge notches fail by the gradual extension of cracks from the notches with localized damage zones, as will be described later. The narrower 3.8 cm wide specimens have a more complex behaviour. Figure 4.15 shows static and low stress fatigue failures of such specimens, indicating the extensive development of damage at the original notch tip. The data in Fig. 4.14 reflect this notch blunting. The stress given in Fig. 4.14 is the net-section stress — the load divided by the cross-sectional area between notches. The static properties show a marked notch sensitivity, giving a net-section strength less than 60% of the UTS. Between one and 10^5 cycles this notch sensitivity is removed by expansion of the damage zone, and the S-N curve remains flat. After 10^5 cycles the S-N curve shifts, running parallel to the unnotched data. In fact, a region of fibres is broken during the development of the extensive damage zone, and if the intact net-cross-sectional area between damage zones was used in calculating the stress, the notched and unnotched sets of data would overlap at low

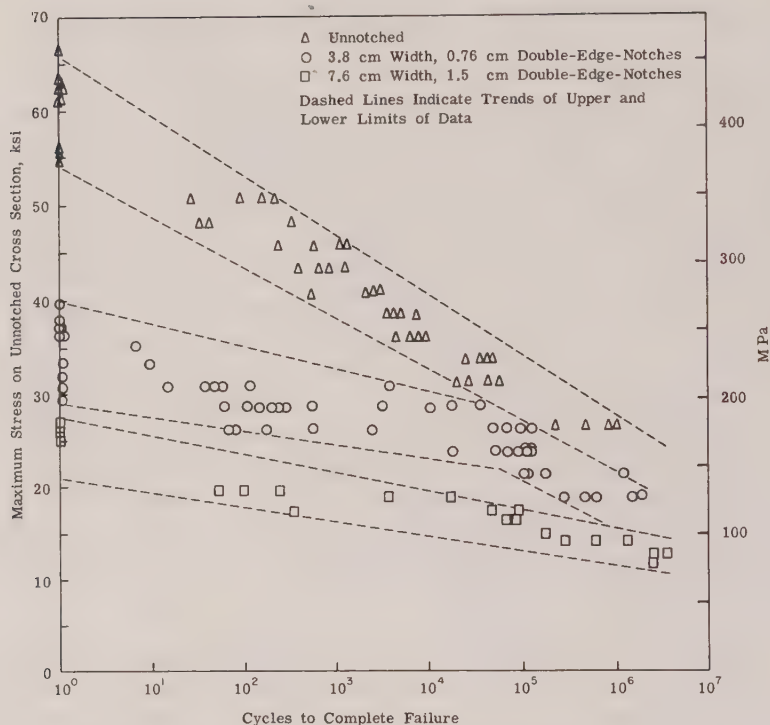


FIG. 4.14 Fatigue life curves for notched and unnotched specimens of $(90^\circ/0^\circ/90^\circ/0^\circ/90^\circ)$ glass/epoxy (from ref. 5).

stresses. The 3.8 cm wide notched specimens are essentially notch-insensitive in low-stress fatigue.

Figures 4.16 and 4.17 show the expansion of the damage zone at the notch tip and the resulting increase in residual load-carrying ability of the specimen due to the reduction in stress concentration, as compared with the decrease in residual strength in the unnotched case. The K/K_Q ratio is the calculated maximum stress intensity factor during cycling divided by the calculated fracture toughness. Since linear elastic fracture mechanics is not applicable over much of this range, this can be taken as the ratio of the applied stress on the specimen in fatigue to the single cycle value at fracture. After a period of cycling, the damage zone size has expanded beyond the size observed in static fracture, and the residual load-carrying capacity at this point begins to increase. Eventually, however, the specimen fails due to the limited lifetime of the net-cross-section. It is remarkable that the gross damage developed at the notch

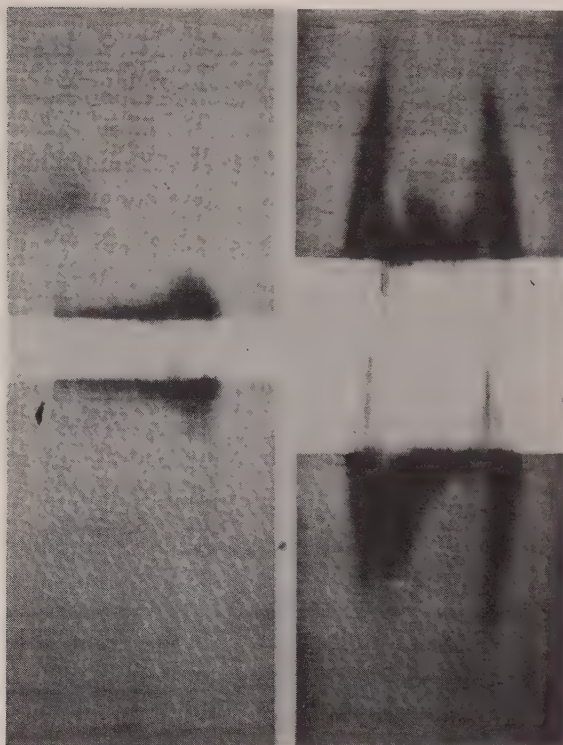


FIG. 4.15 Fractured specimens of 3.8 cm wide notched $0^\circ/90^\circ$ glass/epoxy. Left — static; right — low stress fatigue (from ref. 5).

tip does not greatly interfere with the structural integrity of the net-section, but only serves to remove the effective stress concentration from the notch. The increase in residual strength of notched specimens due to fatigue has been reported widely, first by Waddoups *et al.*⁶⁰ It does not always occur, since extension of the damage zone may severely reduce the net-section area of this specimen geometry in some ply configurations,⁵ offsetting the crack blunting effect; this is obvious for the case of initially notch-insensitive laminates, where there is no static notch sensitivity to be reduced.

4.5.2 Fatigue Crack Initiation and Growth in Notch-sensitive Glass-Fibre Composites

Certain composites such as woven fabric, chopped strand mat and the $0^\circ/90^\circ$ laminate in Fig. 4.14 are very notch sensitive under static loading,

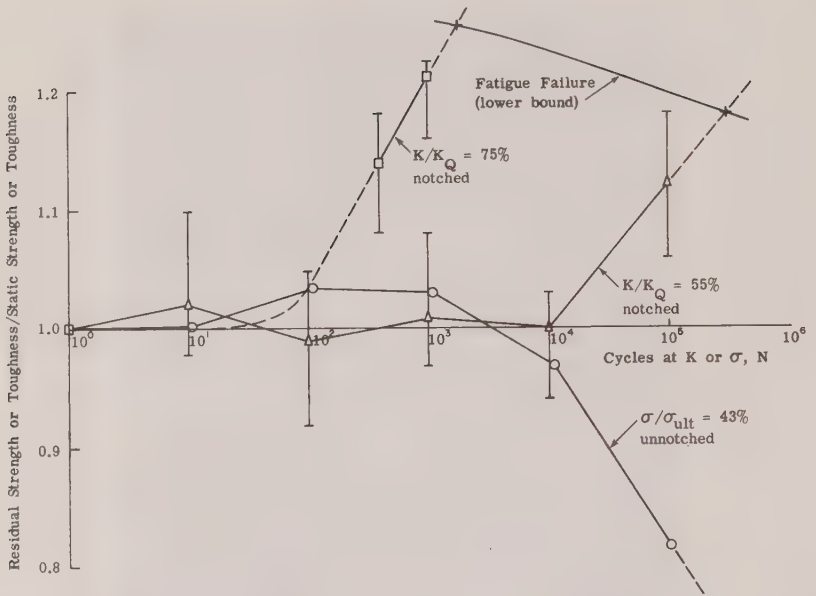


FIG. 4.16 Residual strength and fracture toughness v. number of cycles at various stress and stress intensity levels, 3.8 cm wide 0°/90° glass/epoxy (from ref. 5).

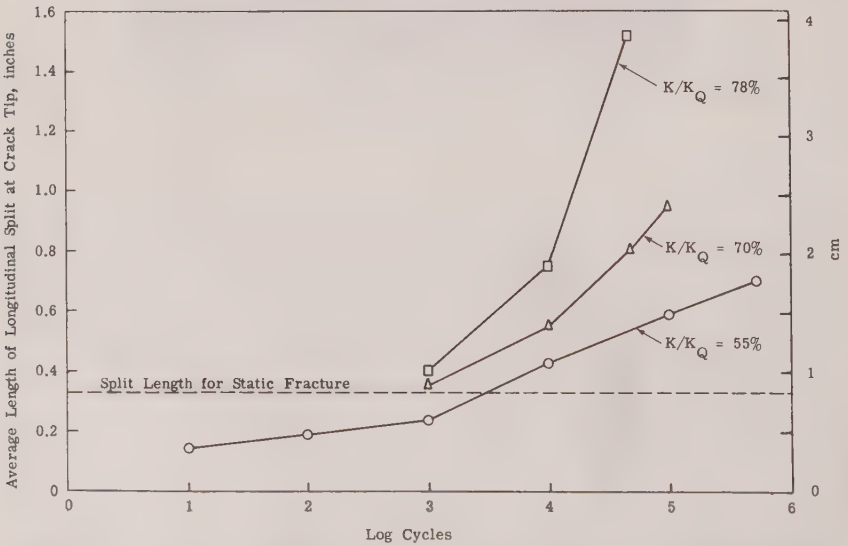


FIG. 4.17 Growth of longitudinal split at crack tip during cycling at various percentages of K_Q , 3.8 cm wide 0°/90° glass/epoxy (from ref. 5).

and will remain so in fatigue if the specimen is sufficiently large. In such cases the propagation of macroscopic cracks in fatigue can be studied in the context of linear elastic fracture mechanics. The subject of fatigue crack growth in composites has been reviewed recently,⁶¹ and the discussion here will be limited.

Figures 4.18 and 4.19 show a mode of trans-fibre crack growth, variations of which are observed in several types of composites.^{28,42} These figures refer specifically to the 0° plies of the 7.6 cm wide $0^\circ/90^\circ$

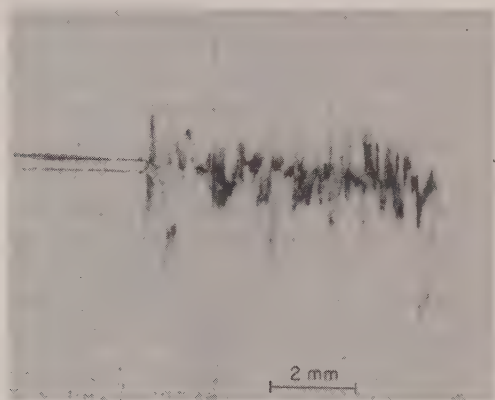


FIG. 4.18 Ligamented fatigue crack advance from notch at left, normal to fibres of 0° ply of 7.6 cm wide $0^\circ/90^\circ$ glass/epoxy specimen (from ref. 28.)

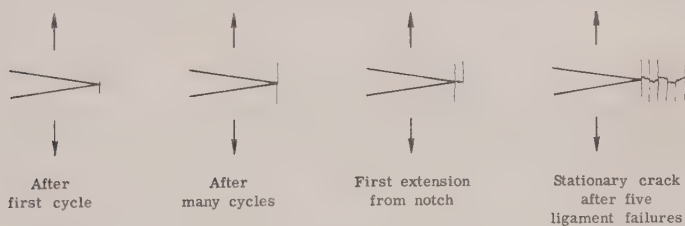


FIG. 4.19 Mode of fatigue crack growth in 0° ply of $(90^\circ/0^\circ/90^\circ/0^\circ/90^\circ)$ laminate, fibres perpendicular to main crack (from ref. 28).

laminate specimens in Fig. 4.14. In these specimens and in the 3.8 cm wide specimens at high stresses, the damage zone remains localized during crack extension, and linear elastic fracture mechanics has been shown to be applicable.²⁸ The mode of crack growth in the 0° plies (the 90° plies simply split parallel to the fibres) is qualitatively identical to

that in static failure,^{6,2} but the extent of the damage zone is greater. The damage zone in the 0° ply consists of a split through the ply, running parallel to the fibres at the notch or at the propagating crack tip; the size and geometry of the damage zone is retained during crack growth. The crack advances in a ligament by ligament mode, remaining stationary as each ligament is fatigued to failure.²⁸ This mode has also been observed in woven fabric, chopped strand mat and SMC composites,^{4,2,6,1} with differing width and length of the ligaments in each case. The ligament in these systems is always a region of the 0° ply or strand rather than a single fibre; the smallest ligaments are of the order of tens of fibre diameters wide. The ligaments in finely woven fabric reinforcement are defined by the yarn diameter, while the rovings of coarsely woven roving reinforcement are broken down into smaller ligaments.^{4,2} The ligament width in chopped strand composites is of the order of the longitudinal strand spacing, but is irregular.^{4,2,6,1}

This mode of ligamented crack growth has proven to be amenable to approximate analysis and prediction, primarily due to the moderate notch sensitivity and large ligaments which limit the severity of the stress gradient in the 0° ply near the crack tip. Defining crack initiation at a notch as the first ligament failure (rather than the first cracking parallel to the fibres), the number of cycles to crack initiation can be predicted by estimating the stress at the notch tip and assuming a UTS/ B ratio of 10 in the first ligament. Following an effective stress concentration approach expressed in fracture mechanics terms for convenience, the stress parallel to the fibres of the first ligament at the notch root, S_1 , is assumed to follow

$$S_1/\text{UTS} = K_1/K_Q \quad (3)$$

where UTS is the static strength of the ligament, K_1 is the maximum cyclic stress intensity factor and K_Q is the fracture toughness.²⁸ Assuming a linear S-N curve for the ligament, the number of cycles to crack initiation should be given by

$$S_1 = \text{UTS} - B \log N_i$$

or

$$\log N_i = (\text{UTS} - S_1)/B = (1 - S_1/\text{UTS})(\text{UTS}/B)$$

so that

$$\log N_i = (\text{UTS}/B)(1 - K_1/K_Q) \quad (4)$$

Figure 4.20 shows good agreement between the prediction in eqn. (4) and experimental data for the $0^\circ/90^\circ$ glass/epoxy system. These data indicate two important points: (1) the assumed relationship in eqn. (3) must be approximately correct, and (2) the ligament at the notch root does follow an S-N curve analogous to that for the unnotched material in Fig. 4.8, with a UTS/B ratio of approximately 10. The larger tensile specimen properties do appear to translate into the properties of the notch root ligament (as they have been shown to translate into single strand properties).

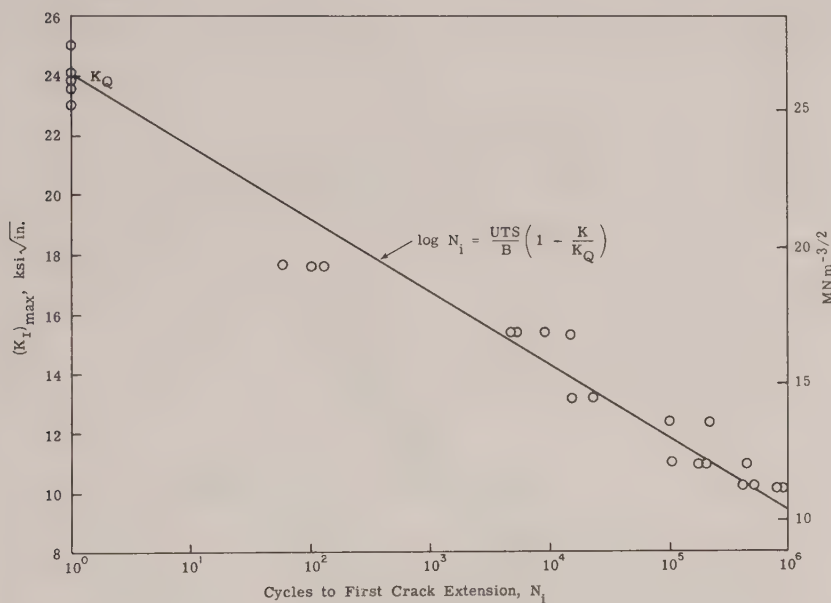


FIG. 4.20 Theoretical v. experimental number of cycles for first crack growth from notch, $0^\circ/90^\circ$ glass/epoxy (from ref. 28).

The model can obviously be extended to the second and subsequent ligament failures to predict the crack growth rate. This could be complicated by cumulative damage effects in these ligaments, which have been stressed at varying levels as the crack tip approached them. Analysis using a cumulative damage law has shown that due to the ligament width and stress gradient, the local stress on the ligament immediately at the crack tip is sufficiently greater than previous stresses so that earlier history has little effect.²⁸ Assuming that cumulative

damage is negligible, the fatigue crack growth rate for a ligament width d reduces to

$$dc/dN = d/\exp[2.3(UTS/B)(1 - K_I/K_0)] \quad (5)$$

where c is the crack length. All of these parameters can be determined experimentally, and have been given for the materials described here in refs. 28 and 61.

Figure 4.21 compares the prediction from eqn. (5) with experimental data for five materials over a range of K_I values and crack growth rates, the latter normalized to ligaments per cycle for the sake of comparison. The UTS/B ratio of 10 for the $0^\circ/90^\circ$ and CSM materials is the value

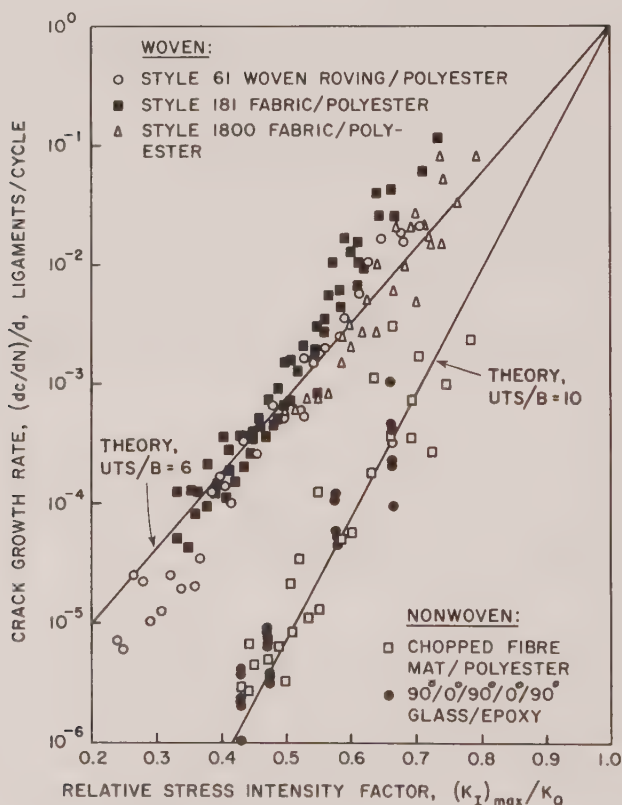


FIG. 4.21 Normalized fatigue crack growth rate curves for five materials (from ref. 42).

given in Fig. 4.9. The ratio of six used for the woven fabric materials is from a curve fit of the high stress, linear portion of their S-N curves, one of which is shown in Fig. 4.11. Both the trend and the absolute value of the data in Fig. 4.21 clearly are in good agreement with the prediction over most of the range. Similar agreement has been demonstrated for SMC⁶¹ and for a combination of woven roving and chopped strand mat reinforcement, under wet and dry conditions.^{50,63}

For the limited class of glass fibre composites which will sustain a macroscopic crack of the type shown in Fig. 4.18, eqn. (5) extends the predictability of fatigue behaviour — given earlier for small regions or specimens — to large scale structures which may fail by the gradual initiation and growth of such a crack from a point of stress concentration. For a given relative loading condition, K_I/K_Q , the only material fatigue parameters present are the ratio UTS/B, inherent in the fibres for non-woven reinforcement, and the ligament width, which depends on the style of reinforcement and is limited to the range of fractions of a millimetre except for chopped strand cases, which may have effective ligaments 10 times larger.^{42,61}

Since many ligaments must be broken, each with the UTS/B ratio of the parent material, the resulting UTS/B ratio for wide notched specimens is higher than for the unnotched case. The experimental data in Fig. 4.21 also fit reasonably well with a power law relationship,²⁸ and this approach has been used by Owen and Cann for similar materials.⁶⁴

4.5.3 Fatigue Crack Growth in Other Composites

Fatigue crack growth in more general cases than described in the last section is usually a difficult process to define.⁶¹ A laminate specimen containing a notch will typically develop an expanding region of interlaminar and transverse ply cracking which cannot be characterized as a single dominant crack. This behaviour is also observed under static loading, where some success has been demonstrated in approximate modelling using numerical methods,⁶⁵ but prediction of such general damage expansion in fatigue has not been demonstrated to the author's knowledge. Some components of the damage, such as interlaminar crack growth, can be studied independently, and have been found to follow a power law crack growth relationship with the local opening and shearing mode stress intensity factors.⁶⁶ Damage at cutouts, although primarily matrix/interface cracking, has been shown to result in a significant number of fibre failures in boron/epoxy laminates.⁶⁷ The build up of interlaminar and transverse ply cracking gradually reduces the stiffness

of the specimen or structure, and can lead to an eventual reduction in residual strength and failure, depending on the severity of the initial notch and the laminate construction.^{5,68,69}

Short-fibre injection moulded thermoplastics are entirely different in their crack growth characteristics than the other composites discussed here. Due to their very short fibres, these materials do not generally sustain the widespread matrix/interface cracking that is common in longer fibre cases, even with very brittle matrices.^{23,55} Failure is usually by a single dominant crack, with a damage zone limited to the order of the length of the long fibres in many cases.⁵⁵ Traditional studies of fatigue crack growth rates can be carried out, and crack growth appears to follow a power law relationship as with unreinforced metals and polymers.^{70,71}

4.6 EFFECT OF LOADING CONDITIONS

Most of the discussion to this point has concerned simple tensile loading, but many composites also suffer similar effects in compression, and multiaxial loading can accelerate damage development in some cases. Compression testing of composites tends to cause difficulties due to buckling and end-brooming problems, and fatigue data may be sensitive to the freedom to delaminate and buckle, either as a unit or ply by ply, which varies with specimen geometry and lateral constraint method. Static longitudinal compressive strengths vary from much lower than the tensile values for aramid and graphite fibres, to higher for boron fibres; transverse compressive strength is generally much higher than transverse tensile strength.⁹ Consistent with the latter observation, the formation of debonding in CSM glass/polyester is found to be suppressed by a more compressive load cycle.⁷²

Constant life diagrams have been reported for glass,^{14,73} graphite^{12,74} and boron^{6,46} laminates which include the effects of varying mean stress and stress amplitude. The effects of compression are not generally much more severe than tension, although confusion due to test methods exists. In specimens without lateral constraint the performance of glass composites in compression was better than that in tension, and similar to that in interlaminar shear; in the same study, graphite laminates gave compression results similar to glass.⁷⁵ Some reports have indicated a more severe effect of compression than tension for graphite composites, particularly for the residual compressive strength,⁷⁴ while others have

not.¹² Flexural fatigue results would seem to be encompassed within the above cases; when tensile failures occur, the flexural fatigue degradation rate is very similar to that in uniaxial tension for SMC.⁷⁶

There are some data available for fatigue under biaxial loading of tubes, as reviewed by Owen.¹⁴ Biaxial tension is particularly severe in the case of CSM glass/polyester, apparently due to the generation of a network of resin cracks; the S-N curve is considerably steeper than in uniaxial tension.⁷⁷

Another aspect of the loading condition is the difference between load and displacement control. Under displacement control the load may drop significantly if the material softens in fatigue, as most polymers³ and composites⁶ do, whether as a result of creep and relaxation or transverse cracking. Under load control (constant load maintained during cycling) the associated strain range increases as the modulus drops, and in some cases, such as short fibres, significant permanent strain may accumulate.^{21,23} A systematic study was carried out by Agarwal and Dally⁷⁸ on the differences between load and strain control for 0°/90° glass/epoxy. A similar S-N curve to that in Fig. 4.8 was obtained in load control; in strain control the curve was almost identical to that, and the degradation rate in both cases (UTS/B in load control) was almost exactly the same.

4.7 FATIGUE LIMITS

The possibility of fatigue limits in composites — stress levels below which fatigue failures do not occur regardless of the number of cycles — is an interesting and controversial topic. While it seems fair to state that most S-N curves given in the literature and obtained using unambiguous test methods show no such limit, not many tests are carried beyond 10^6 or 10^7 cycles. Given the possibilities of behaviour described earlier as non-typical, any decrease in slope of the S-N curve may reflect only a temporary change in failure mechanism, and the S-N curve could continue its descent at longer lifetimes. Those reports of S-N curves which flatten at low stresses, as for some SMC materials,^{29,37} clearly require and demand a great deal more long-term testing of these particular cases. Some of the most interesting and potentially important future materials developments could lie in this area, particularly for glass composites.

It is interesting to speculate as to what might lead to fatigue limits in composites. The unimpregnated strand S-N results for glass fibres

reported earlier were linear up to 10^6 cycles; there is no obvious reason for the curve to flatten out in this simple system. Matrix-dominated properties may have more possibilities, since many polymers are known to show fatigue limits³ which may be associated with a similar phenomenon, the critical strain for craze initiation in environmental stress cracking experiments.⁷⁹ While there are few fatigue data available for polyesters and epoxies, we have found some cases of apparent fatigue limits in very brittle systems in recent, unpublished work, and other data give the same appearance.⁷² Very high fatigue crack growth exponents have also been reported for some epoxies, which suggest very flat S-N curves.^{3,80} However, data on interlaminar fatigue of composites hold little promise of any limits in the matrix-dominated properties of composites⁸¹ except for one set of early, high frequency results.⁸² The very low stresses at which debonding and matrix cracking are initiated in fatigue⁴ also discourage such hopes (Fig. 4.3). The reason for a lack of fatigue limits in matrix-dominated properties could relate to the unknown interface fatigue properties, residual stresses or local very high stress concentration at points of fibre contact or damage, etc.

A related question of the long-term performance of composites has recently come to the attention of at least one industry group.⁸³ Premature failures in unidirectional glass/polyester or epoxy rods used in guy wires or suspension insulators occur with some regularity, typically after several years of service. The mechanical loading is a combination of steady tension and high frequency aeolian wind vibrations. There does not appear to be any severe environmental condition, and electrical effects are not involved. Some failures occur at stresses which appear to be less than 10% of the short term strength (the quality of the rods appears to be very good, and the strength near the cracks is close to the initial strength). The aspect of these field failures which is most unusual is the mode of crack growth. Cracks propagate in a planar fashion perpendicular to the fibres, with no significant splitting or debonding along the fibres. The fracture surfaces are almost perfectly flat over most of the 2cm rod diameter, with fracture surface features which can be traced back to the crack origin, as with many homogeneous materials. Along with the main failure crack, there are often several small cracks which have grown a short distance in from the surface. One such crack is shown in Fig. 4.22 to illustrate the planar mode of crack growth. Attempts to duplicate this mode in the laboratory in tests lasting up to a month produce the normal splitting parallel to the fibres once a high fibre concentration is encountered (Fig. 4.23).

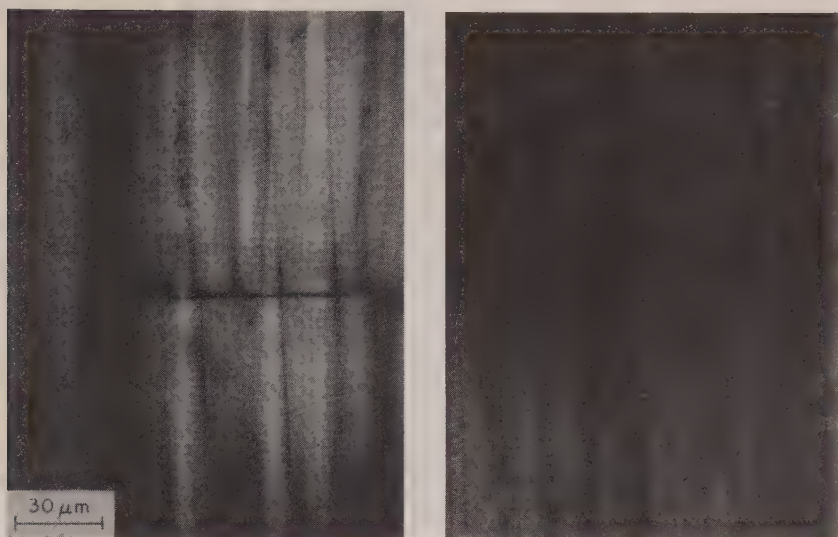


FIG. 4.22 Section through stable crack near fracture surface of field failure in unidirectional glass/polyester rod (left — crack tip; right — along crack, behind tip).



FIG. 4.23 Laboratory test of similar rod to fig. 4.22 with crack growing from right to left through resin layer at surface, then deflecting parallel to fibres when high fibre density is reached.

The only failures of a similar type known to the author are in high modulus (low strain to failure) graphite/epoxy,¹² and in glass composites subjected to corrosive environments.⁸⁴⁻⁸⁶ In the latter case, the corrosive environment appears to attack the fibres at the plane of a matrix crack, producing fibre failures on a precise plane, as in Fig. 4.22, rather than allowing the fibres to fail at weak points along their length, which would produce a rough fracture. The fibreglass rods in question no doubt are exposed to moisture, but moisture generally produces a rough fracture surface because the interface is degraded as well as the fibre.^{63,86} While the failures cited may result from some unknown effect which is restricted to this application, the more unattractive alternative must be considered: glass fibre materials subjected to loading of this type may revert to the extremely brittle failure mode experienced in corrosive environments, if given enough time at low stresses. However, it should be pointed out that the general experience with fibreglass applications in use for long time periods appears to be very good (see, for example, ref. 87).

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Chapter 5

SHEAR PROPERTIES OF LAMINATES

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SUMMARY

Fibre reinforced composite materials have a high specific stiffness and strength. However, the shear properties, which are largely determined by the resin, are lower, of the order of 10 GPa for the modulus and 100 MPa for the shear strength. An appreciation of shear performance enables composite artefacts to be properly designed, loads to be successfully diffused into materials and common errors to be avoided in the mechanical testing of laminates. In this account we consider experimental methods of determining the shear properties of predominantly unidirectional, continuous, fibre reinforced material and compare the results with the theoretical predictions of shear modulus and strength. Using this as a foundation, the performance of laminates and short-fibre, woven and randomly oriented materials is discussed and the effects of fibre surface treatment and voids considered. Finally the important topic of shear fatigue is reviewed.

5.1 INTRODUCTION

Particular interest is attached to the shear properties of composites for two reasons: firstly, shear is the mechanism by which stress is transferred into the fibrous reinforcement in a composite, and secondly, shear

modulus and strength are low compared with other fibre-controlled, longitudinal, mechanical properties. This may limit the potential application of the material or the way in which this application is achieved. For instance, a unidirectional composite containing 60% (volume per cent) of high modulus carbon fibres can have a longitudinal stiffness and strength of 210 GPa and 900 MPa, respectively, compared with a shear modulus and strength of 4.5 GPa and 50 MPa, respectively. Consequently, care has to be taken in diffusing loads into the material and in designing structures subject to shear and off-axis loads.

5.2 NOTATION

The axes used are shown in Fig. 5.1. The 1 or x direction defines the long fibre axis. The 2 or y and 3 or z directions are perpendicular to this axis.

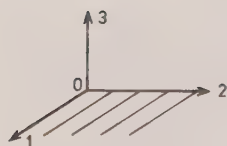


FIG. 5.1 The fibre direction is the 1 or x axis.

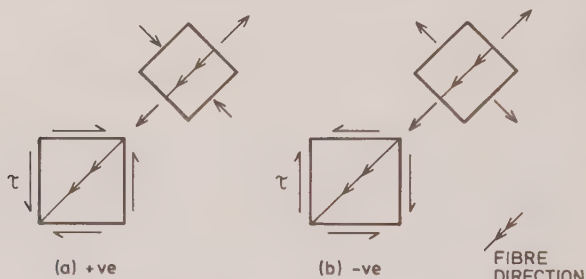


FIG. 5.2 Shear fields with opposite signs.

The shear strains in the 12, 13, and 23 planes are defined thus:

$$\begin{aligned}\gamma_{12} &= \gamma_{21} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} \\ \gamma_{13} &= \gamma_{31} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \\ \gamma_{23} &= \gamma_{32} = \frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\end{aligned}\tag{1}$$

where u , v and w , are displacements in the x , y and z directions, respectively. γ_{12} , etc., in eqn. (1) define true or engineering strains.

Associated stresses are τ_{12} , τ_{13} and τ_{23} . The tensor strain, which is used when transforming axes, is $\gamma_{12}/2$, etc.

Referring to Fig. 5.1 it can be seen that there are three sets of shear modulus, G , and strength, S , to be considered. These are

- G_{12}, S_{12} — in-plane shear deformation
- G_{13}, S_{13} — interlaminar shear deformation
- G_{23}, S_{23} — transverse shear deformation

The distinction between in-plane and interlaminar shear is only made if there is reason to suppose that the structure of the material in the 12 plane is different from that in the 13 plane. A laminate made from successive layers of preimpregnated fibre might show this effect, while the difference would not be expected in a wet moulding.

Pagano and Chou¹ point out that for isotropic materials elastic behaviour is independent of the direction of shear, but that for anisotropic bodies, such as fibre reinforced composites, this is no longer true. This is illustrated in Fig. 5.2. For the shear field in (a) the fibres would be fractured, but in (b) transverse failure would be expected. The authors show the need for a consistent shear stress or strain sign convention if erroneous results are to be avoided when analysing composite structures, especially those for which the fibres do not lie in the direction of applied stress.

5.3 EXPERIMENTAL METHODS OF DETERMINING SHEAR PROPERTIES

Many types of test have been used to measure shear properties, including bar or plate bending, shearing of plates or laminates and the torsional twisting of rods, bars and tubes. Probably the most common, and most criticised, method is the short beam interlaminar shear test in which a thin bar is supported at either end and loaded in the centre, as shown in Fig. 5.3. If W is the load at failure and b and d the breadth and depth, respectively

$$S_{13} = \frac{3W}{4bd} \quad (2)$$

The shear stress is constant with respect to the specimen length but the bending stress is proportional to length. For shear failure to occur before



FIG. 5.3 Short beam shear test.

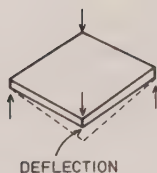


FIG. 5.4 Plate twist test.

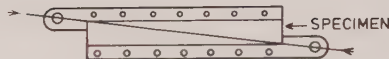


FIG. 5.5 Rail shear test.

flexural failure

$$\frac{d}{2l} > \frac{S}{X}$$

where S is the shear strength, X the bending strength and l the span (effectively the specimen length). Usually a span to depth ratio (l/d) of 5:1 is employed. Support and loading rollers should have a diameter of 3–6 mm to minimise compression damage. The test is discussed in more detail in refs. 2 and 3. Shear failure may occur in the vicinity of the neutral plane usually to one side of the loading point, or may be initiated by transverse compression or transverse tensile delamination at the loading or support rollers, or by tensile failure of the fibres on the underside of the specimen opposite the loading point. In this case the specimen may simply break in two, implying that the shear strength is greater than the calculated value.

Sattar and Kellog⁴ and Kedward⁵ show that the ratio of specimen width to depth has a significant effect on the shear strength measured in a short beam shear test, especially if plies are not unidirectional. As the ratio of dimensions increases, the true shear strength progressively exceeds that calculated from elementary theory. For a unidirectional specimen with a breadth to depth ratio of 2.3:1 the error is 8%. Berg *et al.*⁶ have analysed the test numerically and concluded that the maximum stress is not directly beneath the line of action of the centre load but occurs on two lines at an angle to, and symmetrical about, the loading line.

Specimens consisting of a balanced, symmetrical, lay-up of $\pm 45^\circ$ plies strained longitudinally, or unidirectional material stressed longitudinally at 10° to the fibre axis, have been used to measure modulus and strength by Petit⁷ and Chamis and Sinclair,⁸ respectively. In the former test, strain gauges are fitted along and at right angles to the long axis of the

specimen. Rosen⁹ shows that for the $\pm 45^\circ$ specimen

$$G_{12} = \frac{\sigma_{12}}{2(\varepsilon_{11} - \varepsilon_{22})} \quad (3)$$

and

$$S_{12} = \frac{\sigma_{12}}{2} \quad (4)$$

where ε_{11} and ε_{22} are the strains in the longitudinal and transverse directions. He also notes that because of edge effects care must be taken with the choice of specimen width. In the 10° off-axis test strain gauges are fitted along and at 45° and transverse to the pulling axis and swivel grips are used to avoid constraining the specimen. In a detailed analysis, Chamis and Sinclair consider the effect of misalignment on their results and note that with an angle of 10° between the fibre and pulling axis the major contribution to failure comes from the shear stress.

Hearmon and Adams,¹⁰ Witt *et al.*¹¹ and Tsai¹² have measured the in-plane shear modulus of a homogeneous, orthotropic material by twisting a plate and measuring the deflection at one corner or the centre (Fig. 5.4). In the latter case

$$G_{12} = \frac{3Pl^2}{4h^3w} \quad (5)$$

where P is the load, h the plate thickness, w the deflection and l the side. Care is necessary to keep the deflection small and the plate must be flat initially. The analytical determination of G_{12} depends on the ability of classical laminate theory to describe the deflection of the plate correctly. Some of the difficulties involved in doing this are discussed by Foye.¹³ Johnson¹⁴ demonstrates that it is more difficult to apply the method to $[0^\circ, \pm 60^\circ]$ lay-up samples than to unidirectional or $[0^\circ, 90^\circ]$ material. Hua¹⁵ has used strain gauges to obtain the deflection, being careful to measure the strain in tension and compression in case properties are not the same in the two cases.

A more widely used test method for laminates is the rail shear test (Fig. 5.5). The specimen is secured between two metal rails in such a way that either rail protrudes beyond one end of the specimen. The jig is loaded in compression with either the line of action passing diagonally through opposite corners of the plate, or through the centre line of the specimen. Strain gauges at $\pm 45^\circ$ are fixed to the centre of the specimen.

Whitney *et al.*¹⁶ examined the test theoretically and experimentally in some detail and deduced the ratio of length to breadth, l/b , to obtain uniform shear at the centre. Usually if this ratio exceeds 10:1 the shear stress is substantially uniform. Only for $\pm 45^\circ$ laminates is this not so, though even in this case experimental work showed that measured moduli agreed with calculated values. The existence of large stresses at the corners of the plate may cause premature failure in a non-shear mode leading to excessively low values of shear strength for $\pm 45^\circ$ laminates. Garcia *et al.*,¹⁷ using finite element methods, suggest that there may be an optimum l/b ratio for a specific material which leads to uniform shear in the centre of the specimen and minimises stress concentration at the corners. They note that this may require $l/b=6:1$ rather than 10:1 or 12:1. In addition it was found that it made very little difference whether the loading was diagonal or along the centre line.

The most direct way of obtaining a uniform shear stress field in a specimen is to twist a thin walled tube about its long axis, taking care to ensure that the specimen is not restrained in an axial direction. In practice it is easier to use a solid rod turned to a diameter. A square cross-section specimen, 150 mm in length, with the centre 100 mm turned to a diameter of approximately 6.3 mm has been successfully used.¹⁸ The specimen is mounted between two accurately aligned, four-jaw, self-centring chucks, one of which is free to move longitudinally. One chuck is rotated at a constant rate of 0.5 rad min^{-1} , and the torque transmitted by the specimen recorded by an arm attached to the free chuck which actuates a load cell. The shear modulus, G , is obtained from the initial slope of the torque twist curve using the equation

$$G = \frac{32T}{\theta \pi d^4} \quad (6)$$

where T is the torque, θ the angle of twist per unit length and d the rod diameter. Typical torque twist curves are shown in Fig. 5.6. Failure is said to have occurred when either the torque is parallel to the abscissa, when all the material is assumed to be stressed to the same level, or when there is a sudden discontinuity indicating cracking in the outer layers of the specimen. In the former case the shear strength is given by

$$S = \frac{12T}{\pi d^3} \quad (7)$$

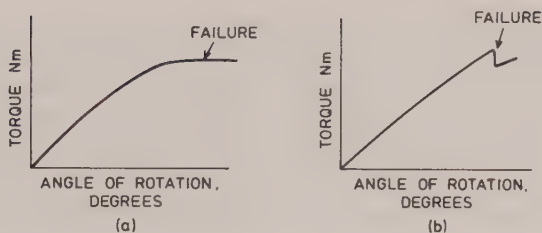


FIG. 5.6 Torque twist characteristics; (a) 'plastic' (b) 'brittle' type failure.

and in the latter by

$$S = \frac{4}{\pi d^3} \left(\theta \frac{dT}{d\theta} + 3T \right) \quad (8)$$

where the meanings of $\theta(dT/d\theta)$ and T are shown in Fig. 5.7. Equation (8) allows for non-linearity in the torque twist curve.

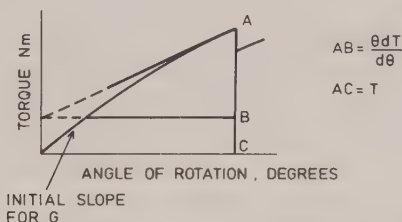


FIG. 5.7 Details required for calculation of shear modulus and strength.

Phillips and Scott¹⁹ have shown that the foregoing analysis sometimes predicts a higher stress than that for failure at the specimen surface, at an angle of rotation less than the failure angle. When a failure does occur, the maximum shear stress is not at the surface of the specimen. This is believed to be partly due to plastic deformation in the matrix but, in addition, to partial fibre resin debonding in the vicinity of the surface.

The torsion rod or tube specimen is free to move axially in the testing machine but tensile and compensating compressive stresses still arise because material at the periphery of the specimen is subject to twist and hence elongation occurs. Phillips and Scott¹⁹ have analysed the effect and noted that for unidirectional carbon fibre composites the increase in shear stress is no more than 1.5% and may be ignored.

Torsion tests on solid rods have been criticised on the grounds that the

shear field is not constant over the cross-section, but a maximum at or in the vicinity of the surface, the inner part of the specimen may exert some constraint on the outer layers and failure may be initiated at small surface flaws. Chiao *et al.*²⁰ recently made measurements on thin walled tubes and solid rods made from the same material (65% aramid fibre epoxy resin) and, within the limits of the experimental error, found no difference in the shear parameters determined using the two types of specimen.

So far in discussing the solid rod torsion test we have assumed that all the fibres lie along the long axis of the rod and that the value of G measured is G_{12} . The shear behaviour of materials in torsion is complex and it is necessary to examine the situation in a little more detail for other fibre alignments. Assuming that the long axis of the rod is in the 1 direction of Fig. 5.1, ref. 21 shows that the shear strains have the following values: $\gamma_{12} = \gamma_{13} \neq 0$, $\gamma_{23} = 0$. If a round bar is composed of unidirectional fibres in the 1 direction, twisting the bar in the 23 plane involves deformation in the 12 and 13 planes and ref. 22 shows that the modulus measured is $2(G_{12} \times G_{13}) / (G_{12} + G_{13})$. If we assume that $G_{12} = G_{13}$, the modulus measured in a torsion rod test with the fibres in the direction along the rod axis is G_{12} . If the long axis of the bar is in the 3 direction, but the fibres are still in the 12 plane and the rod is twisted in the 12 plane, deformation involves G_{13} and G_{23} and the modulus measured is $2(G_{13} \times G_{23}) / (G_{13} + G_{23})$, enabling the transverse shear modulus to be determined if G_{13} is known.

Goggin²³ and Stoffler²⁴ discuss torsion measurements on rectangular bars. This geometry is convenient for dealing with laminates. Wall and Card²⁵ deal with shear measurements on filament wound, helical, glass fibre epoxy tubes. They noted that shear moduli were in good agreement with calculated values.

5.4 THEORIES OF MODULUS AND STRENGTH

5.4.1 Unidirectionally Reinforced Materials

Ashton *et al.*²⁶ give a concise summary of the methods available for predicting the elastic properties of composites. It is useful to recall that most methods require that the fibre and matrix are linearly elastic and homogeneous, free of voids, with complete bonding between the components, that the fibres are regularly spaced and aligned and the material is initially stress free. Since few of these requirements are ever completely

met, the excellent agreement frequently noted between theory and experiment can be surprising.

Hashin and Rosen²⁷ used a variational method to bound G_{12} and G_{23} , noting that in the former case the bounds coincided. Among the authors attempting exact solution are Heaton,^{28,29} and Sendeckyj.^{30,31} The former considered a square array of fibres, the latter a more complex arrangement which led to good agreement between theory and experiment up to a volume loading of 70% fibre. Adams and Doner³² employed a numerical method to calculate the longitudinal or in-plane shear modulus and shear stress concentration factor due to the presence of fibres, as a function of the ratio of fibre to resin shear modulus and fibre volume loading. Square and hexagonal fibre arrays were considered. Halpin and Tsai²⁶ suggested, after studying a generalisation of the self consistent field method, that the shear modulus could be represented by an equation of the form

$$\frac{\bar{G}}{G_m} = \frac{(1 + \zeta \eta V_f)}{(1 - \eta V_f)} \quad (9)$$

with

$$\eta = \left(\frac{G_f}{G_m} - 1 \right) \left/ \left(\frac{G_f}{G_m} + \zeta \right) \right.$$

where $\bar{G} = G_{12}$ or G_{23} ; G_f and G_m refer to the shear moduli of the fibre and matrix, respectively; V_f is the fibre volume fraction and ζ is a measure of the reinforcement. Reliable estimates of ζ can be obtained by comparing the results of eqn. (9) with numerical or experimental results. As a first approximation for calculating G_{12} a value of unity is used. Hewitt and de Malherbe³³ deduced an empirical expression for ζ from curve fitting. They found that

$$\zeta = 1 + 40 V_f^{10} \quad (10)$$

noting that this gave the correct value for $\bar{G}$ for $V_f = 0, 1$ and gave excellent agreement for a unidirectional E-glass polyester resin composite over the range $V_f = 0.4 - 0.75$ with a maximum discrepancy of 10%.

If $\zeta = 0$, eqn. (9) reduces to the constant stress estimate for $\bar{G}$

$$\frac{1}{G} = \frac{V_f}{G_f} + \frac{V_m}{G_m} \quad (11)$$

If $\zeta = \infty$, eqn. (9) reduces to the constant strain estimate of $\bar{G}$

$$\bar{G} = V_f G_f + V_m G_m \quad (12)$$

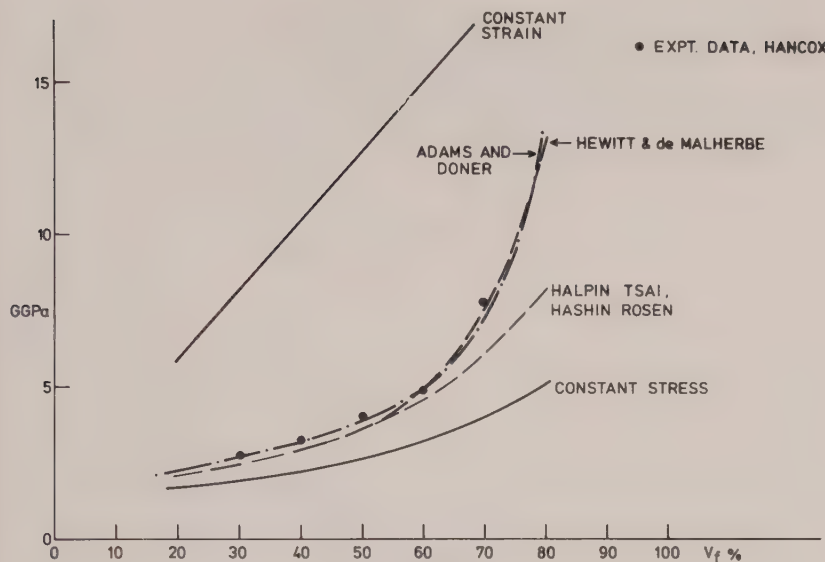
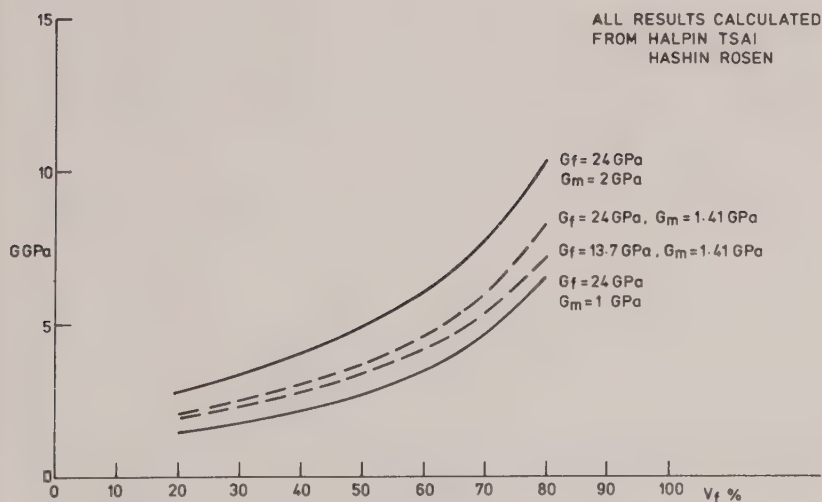
With $\zeta = 1$, eqn. (9) becomes

$$\frac{G_{12}}{G_m} = \frac{(G_f + G_m) + (G_f - G_m)V_f}{(G_f + G_m) - (G_f - G_m)V_f} \quad (13)$$

the result obtained in ref. 27 for a hexagonal array of circular fibres.

To use any of these equations to predict shear modulus it is necessary to know values of G_f and G_m . Dean and Turner³⁴ measured the stiffness constants of high strength (HTS) and high modulus (HMS) unidirectional carbon fibre epoxy resin composites by ultrasonic means and then, by choosing fibre properties, fitted their data to the results predicted by ref. 27. For HMS fibre, $G_{12} = G_{13} = 13.7$ GPa and $G_{23} = 2.8$ GPa. For HTS fibre, $G_{12} = G_{13} = 24$ GPa and $G_{23} = 5.5$ GPa, reflecting the less ordered structure of the high strength fibre. Adams,³⁵ employing a torsion pendulum operating between 0.01 and 0.1 Hz found that $G_{12} = G_{13} = 14$ GPa for HMS carbon fibres and $G_{12} = G_{13} = 17.5$ GPa for HTS carbon fibres. Pitch-based carbon fibres had a longitudinal shear modulus of approximately 18 GPa. Recently Srinwasagopal³⁶ has used a vibrational technique with carbon fibres and found that between 0.5 and 1.5 Hz, $G_{12} = 9$ GPa for mesophase pitch fibre and $G = 35$ GPa for HMS fibres. For epoxide and polyester resins the static shear modulus lies between about 1 and 2 GPa. Specifically Smith *et al.*³⁷ quote $G = 1.41$ GPa for an anhydride cured epoxide resin with a short cure at 120°C and $G = 1.19$ GPa for a similar resin with a longer cure at 140°C. In Fig. 5.8 the constant strain and constant stress models and the results of refs. 26, 27, 32 and 33 have been used to calculate the variation of shear modulus G_{12} for unidirectional carbon fibre composites made from HTS fibre ($G_f = 24$ GPa) and epoxide resin ($G_m = 1.41$ GPa). The experimental results, for the above system, are from ref. 18. Agreement between the results and the numerical solution of the elasticity equations³² is very good. The Halpin-Tsai equation, modified above 55% fibre by ref. 33, also gives reasonable agreement. Figure 5.9 shows the effect of assuming different shear moduli for the resin (1 and 2 GPa) with HTS carbon fibre, and of taking different fibre moduli (13.7 and 24 GPa) with a matrix shear modulus of 1.41 GPa.

The numerical analyses of refs. 32 and 38 enable the stress concentration, which occurs at the point of nearest approach of two fibres,

FIG. 5.8 Shear modulus v. V_f .FIG. 5.9 Shear modulus v. V_f .

to be predicted. Values are shown in Fig. 5.10. The results of Adams and Doner are for HTS and HMS fibres in a square array, and it can be seen that the stress concentration is worse with the higher shear modulus carbon fibres. Heaton's results are for HTS carbon fibres in a square and a hexagonal array. Fibre and matrix shear moduli had the same values

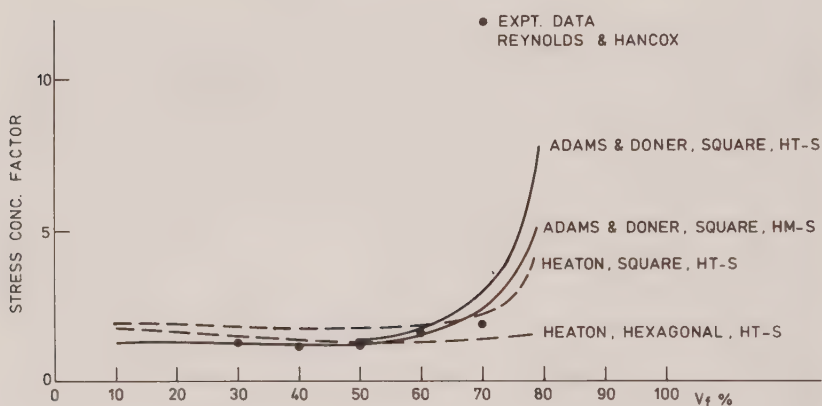


FIG. 5.10 Stress concentration factor *v.* V_f .

as previously referred to ($G_f = 24$ GPa, $G_m = 1.41$ GPa). The experimental results from ref. 39, for $50\%_o$ and above of fibre, lie on or between the limits given by Heaton. This may reflect the changing fibre array as the fibre content increases. Below $50\%_o$ fibres, the deviation between theory and experiment is probably due to stress relief by plastic flow of the matrix transferring stress to the fibres.

The most rigorous estimation of the strength of unidirectionally reinforced material has been made by Shu and Rosen,⁴⁰ who obtained upper and lower bounds for the longitudinal, S_{12} , and transverse, S_{23} , shear strengths using the methods of limit analysis of plasticity. The fibres are assumed to be elastic-brittle and rigid, and the matrix elastic-perfectly plastic and obeying von Mises' yield criterion. It is shown that S_{12} can be increased by 27% above the matrix shear strength as $V_f \rightarrow 1$. For S_{23} the bounds are much further apart and $S_{23} \rightarrow \infty$ as $V_f \rightarrow 1$. It is concluded that there is much more scope for increasing S_{23} by the incorporation of reinforcing fibres than there is for increasing S_{12} . Experimental results for S_{12} for HTS and HMS fibres, taken from ref. 18, are shown in Fig. 5.11, together with the upper limit according to ref. 40.

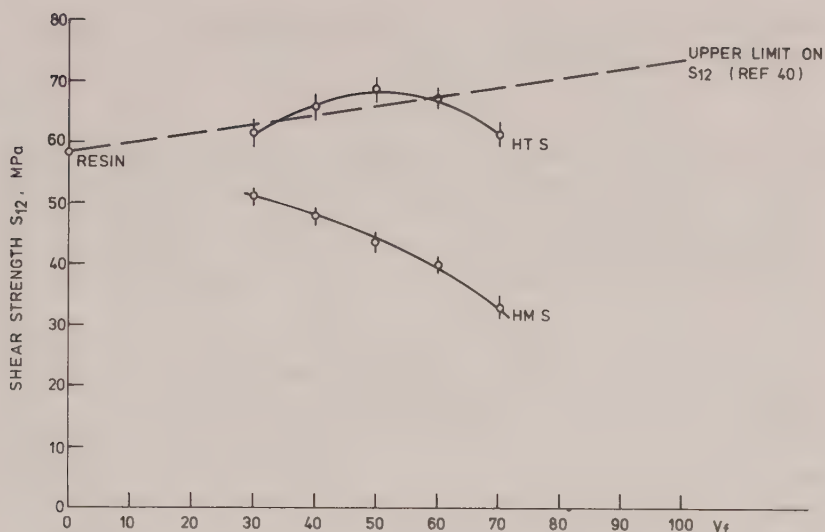


FIG. 5.11 The shear strength of unidirectional carbon fibre composites.

Predicted and experimental values for HTS material are in tolerable agreement up to 60% V_f , when the real shear strength begins to decrease — probably because of the large stress concentration that occurs between fibres. Results from HMS material are believed to be lower because of poorer bonding between the fibre and resin.

Reynolds and Hancox³⁹ assumed that the maximum shear stress in a fibre composite was βS , where β is a stress concentration factor due to the presence of fibres. For failure, the maximum stored strain energy must be sufficient to initiate and propagate a crack. If the bond between the fibre and resin is sufficiently good, so that failure occurs in the resin rather than at the interface, then we have

$$\frac{\beta^2 S_{12}^2}{G_{12}} = \frac{S_m^2}{G_m} \quad (14)$$

where the subscript m refers to the matrix and β is unity for the unreinforced resin. Physically $S_{12} > S_m$ because good bonding leads to a stiff material and until sufficient strain energy is stored failure cannot occur. For less-well-bonded material eqn. (14) holds but with a smaller, unknown quantity on the right-hand side. If S_m and G_m are known, together with values of G_{12} and β it should be possible to calculate S_{12} for well-bonded material.

The most elementary way of estimating shear strength is to assume that a rule of mixtures applies,⁴¹ then

$$S_{12} = x_i S_i + (1 - x_i) S_m \quad (15)$$

where S_i is the shear strength of the interface and x_i the fraction of the fracture area which is interface. In ref. 41 the equation is used to deduce a value of S_i from the data for S_{12} . If x_i is taken as proportional to V_f and $S_i < S_m$, eqn. (15) would approximately model the form but not the magnitude of the shear strength results for HMS composite given in Fig. 5.11.

Some representative values for shear modulus and strength for various types of unidirectional fibrous reinforcement are listed in Table 5.1. The values can only be taken as a guide to what can be obtained, since they will depend on the exact type of fibre and resin, the skill with which the composite was fabricated, and the test method. Most of the measurements were obtained from solid rod torsion tests. Shear strengths from the short beam test could well have values up to 100 MPa or more.

TABLE 5.1
SHEAR PROPERTIES OF UNIDIRECTIONAL COMPOSITE EPOXY MATERIALS

<i>Material</i>	G_{12} (GPa)	G_{23} (GPa)	S_{12} (MPa)
60°/° HTS carbon	4.8–5.5	2.0	68
60°/° HMS carbon	4.2	1.1	42
60°/° aramid	2–5	—	31
60°/° E-glass	4.5–5.2	—	63
60°/° S-glass	5.6	—	90
60°/° boron	6.5–6.9	—	80

5.4.2 Laminated Materials

The properties of anisotropic materials vary with the direction considered in the specimen (see ref. 26 for full details). The shear modulus of a 60°/° unidirectional HTS carbon fibre composite lamina as a function of θ , the angle between the direction considered and the longitudinal fibre axis, is shown in Fig. 5.12. The maximum value of G_{xy} occurs at 45° and the curve is symmetrical about this angle.

Many composite structures are made up by stacking sheets of pre-impregnated fibre such that each sheet has a specified orientation with respect to a reference direction. This enables improved properties to be

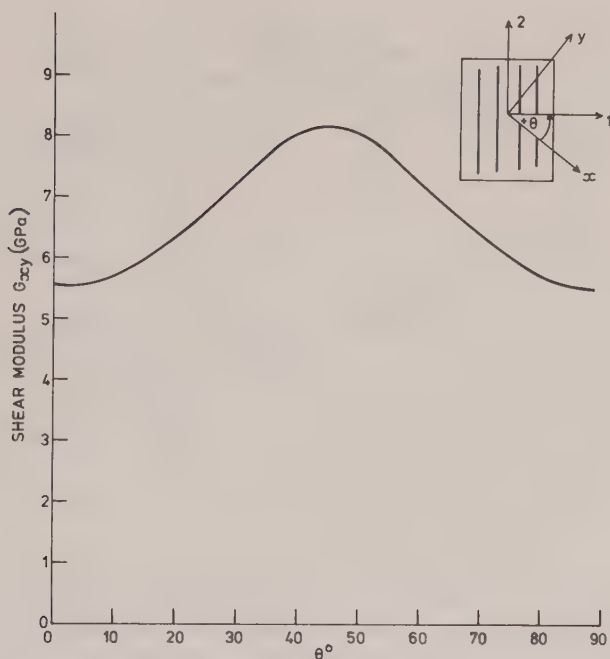


FIG. 5.12 Variation of G_{xy} with θ for $60^\circ/0$ HTS carbon fibre ply ($E_{11}=148$ GPa, $E_{22}=9$ GPa, $G_{12}=5.52$ GPa, $\nu_{12}=0.3$).

obtained in off-axis directions. Typical stacking sequences are $[0^\circ, 90^\circ]_s$, $[\pm 45^\circ]_s$, $[0^\circ, \pm 60^\circ]_s$ and $[90^\circ, \pm 45^\circ, 0^\circ]_s$, where the subscript s signifies a lay-up that is symmetrical about a centre plane. Symmetrical lay-ups are commonly used because tensile loading then does not cause bending of the laminate. It is possible to calculate the elastic properties of a laminate by taking the elastic constants for rotated laminae (as is shown for the shear modulus in Fig. 5.12) and summing in the appropriate manner. The mathematical details are described in refs. 26 and 42. Generalised computer programs are readily available to ease the work. Calculated values of G_{12} for GRP and CFRP $60^\circ/0$ laminates are given in Table 5.2. As would be expected, the $[\pm 45^\circ]_s$ lay-up has the largest shear modulus.

It is possible to deduce the shear strength of a laminate by applying a shear stress and calculating the general stresses and strains in individual plies. A failure criterion must be specified, e.g. maximum stress or strain (Tsai–Hill, Tsai–Wu),^{4,2} and the applied stress incremented until failure

TABLE 5.2
COMPUTED SHEAR MODULI FOR LAMINATES
(a) $60^\circ/\circ$ GRP, E_{11} (longitudinal modulus) = 43.4 GPa,
 $G_{12} = 4.78$ GPa

<i>Lay-up</i>	(G_{12}) laminate (GPa)
$[0^\circ, 90^\circ]_s$	4.78
$[\pm 45^\circ]_s$	12.0
$[0^\circ, \pm 60^\circ]_s$	8.4
$[90^\circ, \pm 45^\circ, 0^\circ]_s$	8.4

(b) $60^\circ/\circ$ HTS CFRP, $E_{11} = 148$ GPa, $G_{12} = 5.52$ GPa.

<i>Lay-up</i>	(G_{12}) laminate (GPa)
$[0^\circ, 90^\circ]_s$	5.52
$[\pm 45^\circ]_s$	38.0
$[0^\circ, \pm 60^\circ]_s$	22.0
$[90^\circ, \pm 45^\circ, 0^\circ]_s$	22.0

occurs in one ply. The process can be repeated until all plies have failed but the definition of laminate failure is arbitrary. It may be that for a given applied shear stress the first ply failure occurs in transverse tension or compression rather than by shear failure. Ideally, non-linearity in the matrix-controlled stress-strain properties should be allowed for. The approach is best handled by a computer, and depends critically upon the values used for the various elastic and strength properties and a full appreciation of the effects of thermally induced strains and water on the mechanical properties. The work thus rests firmly on the foundation laid in Sections 5.3 and 5.4.1, where methods of measuring and predicting shear properties for unidirectional materials were discussed. Some measured shear strengths and moduli for laminates are given in Table 5.3. For both $[0^\circ \pm 45^\circ]_s$ and $[90^\circ, \pm 45^\circ, 0^\circ]_s$ laminates the in-plane shear modulus increases with the number of 45° plies.

5.4.3 Short Fibre, Woven and Randomly Oriented Materials

Many very useful composite materials comprise a resin matrix reinforced with short fibres aligned or randomly oriented in a plane (e.g. aligned carbon fibre felts, chopped glass strand mat); mixtures of randomly oriented short, or continuous, fibres in a matrix which may be heavily loaded with particulate matter (e.g. moulding compounds such as SMC, HMC), or woven glass rovings; or short fibres randomly oriented in three dimensions (moulding compounds such as BMC). Cox⁴³ has deduced the

TABLE 5.3
MEASURED SHEAR STRENGTHS AND MODULI FOR LAMINATES

Material	S_{12} (MPa)	G_{12} (GPa)
60°/0 HTS epoxide [±45°] _s	210	33.8
60°/0 HTS epoxide [0°, ±45°] _s	241	17.2
60°/0 HMS polyimide [±45°] _s	207–264	29–31
60°/0 HMS polyimide [90°, ±45°, 0°] _s	197–260	18

in-plane shear modulus of a random two-dimensional fibre array. He found that

$$G_{12} = \frac{E_f V_f}{8} \quad (16)$$

with a Poisson's ratio of 1/3.

Similarly, for a three-dimensional random array

$$G = \frac{E_f V_f}{15} \quad (17)$$

with a Poisson's ratio of 1/4.

The derivations ignore any contribution from the matrix.

Halpin and Pagano⁴⁴ have shown that the properties of a two-dimensional material can be modelled using laminate theory. Layers of unidirectional composite are stacked together with the volume fraction and orientation of each layer governed by the percentage of fibres at each orientation in the physical system. For 50°/0 glass fibres modelled as a [90°, ±45°, 0°]_s laminate they find that $G_{12} = 7.45$ GPa as against 4.4 GPa from eqn. (16). Woven rovings could be analysed to a first approximation as a [0°, 90°]_s laminate. The results quoted in Table 5.2 indicate that G_{12} should be the same as for unidirectional material.

Chamis⁴⁵ has presented a semi-empirical analysis of the properties of two-dimensional random materials, while Halpin⁴⁶ has noted that G_{12} for short aligned fibres is given by eqn. (9) with $\zeta = 1$.

Some measured and calculated moduli and strengths are listed in Table 5.4. Several points should be noted. In-plane shear strength, S_{12} , is much larger for glass fibres than S_{13} or interlaminar shear strength, as

TABLE 5.4

MEASURED AND CALCULATED SHEAR PROPERTIES OF CHOPPED STRAND MAT,
WOVEN ROVING AND RANDOM FIBRE COMPOSITES

(a) Measured				
<i>Material</i>	V_f	$G_{12}(\text{GPa})$	$S_{12}(\text{MPa})$	$S_{13}(\text{MPa})$
CSM	15	2.76	—	—
CSM	15–25		62–96	22–29
WR	35	3.6	—	—
WR	30–40		94–110	—
WR	30–45		—	11–28
SMC	15	4.2	—	—
SMC	35	6.3	—	—
Unidirectional short HTS fibre	51		—	65
HMS fibre	52		—	42
(b) Calculated				
CSM	15	1.3	(eqn. 16)	
SMC	15	1.3	(eqn 16)	
SMC	35	3.1	(eqn 16)	
WR	35	2.8	(laminate theory)	
2D random S glass	60	13.8	—	
2D random HTS carbon fibre	60	27.6	—	
2D random B fibre	60	37.9	—	

Note: CSM = chopped strand mat, WR = woven rovings, SMC = sheet moulding compound. Data for chopped and woven glass fibre are from ref. 47, SMC data from ref. 48, short carbon fibre data from ref. 49 and random fibre data from ref. 45.

the latter involves shear deformation between sheets of material rather than within the sheet. The results for carbon fibres are similar to those obtained for continuous aligned material. In-plane shear moduli calculated from eqn. (16) are low, probably because the calculation ignores any contribution from the matrix.

5.5 FIBRE SURFACE TREATMENT

For some years it has been customary to add a coupling agent, often a silane, to the surface of glass fibres to improve the fibre resin bond

strength. Different agents specific to given resins are available. The improvement in bond strength, and hence in interlaminar shear strength, is particularly noticeable if specimens are exposed to humid conditions and mechanical properties measured. Further details of coupling agents for glass fibres are given by refs. 50, 51 and 52 (see also Table 1.1, Chapter 1).

It was noted when carbon fibre composites were first produced that the shear properties were very low, and a considerable amount of work was devoted to developing surface treatments for the fibres which would improve the bond strength. Successful methods were developed based on oxidation in a solution of hypochlorite⁵³ and in hot air.⁵⁴ Unlike other treatments these do not reduce the fibre strength. Surface treatment typically raises the interlaminar shear strength of 60%_o unidirectional HTS fibre composite from 40 to 70 MPa, and that of HMS composite from 17 to 45 MPa. Most carbon and glass fibres are currently used in the surface-treated condition.

5.6 VOIDS

Since shear properties are strongly influenced by those of the matrix, voids, up to 3% of which are frequently present in composites, have a marked effect on mechanical properties. Judd and Wright⁵⁵ quote a percentage fall-off in the interlaminar shear strength for 1% of voids of $7 \pm 1\%$ for GRP, $6 \pm 4\%$ for CFRP, rising to 21% for carbon fibre polyimide composites. Hancox⁵⁶ noted that 5% of voids caused a fall-off in the shear strength of CFRP of 30% but with the fastest rate of fall for the first 1% of voids. Results for the in-plane shear modulus of CFRP⁵⁷ showed an initial slow decline up to 1.5% voids and then an accelerating fall until at 3% voids G_{12} had been approximately halved. Thereafter the reduction in properties was much slower.

Various attempts have been made to predict the fall-off in properties. Foye⁵⁸ considered a cylindrical array of voids, Greszczuk⁵⁹ used a strength of materials approach for spherical and cylindrical voids and Corten⁶⁰ assumed that the void could be replaced by an effective crack of length equal to the cube root of the void volume. All three models are in reasonable agreement with the results of ref. 57 on CFRP up to approximately 1% of voids but then all indicate a larger remaining shear modulus than is found experimentally. Difficulties arise in compar-

ing theory and experiment because the void content will vary throughout the specimen and voids have a spectrum of sizes and shapes.

5.7 SHEAR FATIGUE

No account of the shear properties of laminates is complete without a brief mention of fatigue behaviour. Green and Pratt⁶¹ studied the interlaminar shear fatigue behaviour of unidirectional CFRP and observed an initial 10% decrease in shear strength followed by a region of essentially constant strength between 10^2 and 10^6 cycles. Failed specimens showed tensile and multiple shear failure or simply multiple shear failure, depending on the batch of fibre used in specimen preparation, with little or no bond failure. It was concluded that it was the resin matrix which was the critical component in the interlaminar shear fatigue process.

Other workers, including Beaumont and Harris⁶² and Novak⁶³ (who used square cross-section specimens), Simon and Barnet⁶⁴ (half ring specimens) and Phillips and Scott¹⁹ (round, solid rods) have studied the shear fatigue behaviour of unidirectional composites. All these workers found a very marked decrease in shear properties, with specimens failing at half the static strength after 10^3 cycles. The results were similar whether carbon, glass or aramid fibres were used, even though the static shear behaviour of the first two is non-linear, while that of an aramid composite is linear to failure. If the shear strain amplitude is constant, the shear stress initially decreases linearly with the logarithm of the number of cycles. Eventually, after a characteristic lifetime, cracks propagate along the specimen, leading to a rapid decrease in the torque sustained for a constant shear strain. Under constant torque amplitude cycling the compliance of the specimen increases steadily until cracking occurs, causing total failure. The shear modulus of the unreinforced resin is constant under repeated loading until catastrophic failure occurs. It is believed that this indicates that the initial slow decrease in properties of a composite is due to debonding. There is evidence¹⁹ that at very small shear strain amplitudes debonding does not occur but shear fatigue may still take place because of matrix cracking. Novak⁶³ noted discrete cracking in the matrix of a boron-epoxide composite. There are thus considerable differences in shear fatigue behaviour under interlaminar and torsional stressing conditions. In the former case it appears that the matrix governs failure and the decrease in properties is slow, while in the

latter case fibre debonding is believed to occur initially and the decrease in properties is very rapid.

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Chapter 6

MACHINABILITY OF LAMINATES: PUNCHING AND DRILLING

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SUMMARY

In contrast with metals, there is very little workshop experience and research relating to the machining of reinforced plastics. This chapter discusses established machining techniques, cutting tool materials and novel cutting techniques such as jet-cutting and laser machining.

Printed circuit boards (PCBs) constitute the largest volume of machined reinforced plastics materials and are considered in some detail. The key operation in PCB machining is hole production, whether by drilling or punching, and the PCB industry's requirements in this field have generated a significant volume of research. Drill bit design and performance are discussed, together with the selection of cutting speeds and feeds, and developments in drilling machine design are outlined. Economic factors affecting the choice between drilling and punching are considered.

The shearing process is described, with discussion of machine-tool design, its dynamic response to loading and an analysis of the stages of the shearing itself. The problems of laminate stripping and of punch hole quality assessment are explained.

6.1 THE MACHINABILITY OF REINFORCED PLASTICS

6.1.1 Introduction

One of the most important factors determining whether reinforced plastics are widely used is their behaviour during machining operations

such as cutting, drilling and punching. This chapter differs from many discussions of laminate properties in that it is not concerned with a single, isolated property such as (for instance) fracture toughness, although fracture toughness undoubtedly has an important part to play in determining machining behaviour. The present discussion is about the behaviour of laminates in situations where several properties become important simultaneously.

The machining of metals has been a subject of great interest, and extensive research, for nearly a century. This activity has led to wide general appreciation of 'good' cutting methods for metals, under most orthodox machining conditions, but reinforced plastics have received comparatively little attention. This chapter seeks to summarise what has been done so far, with special reference to printed circuit boards, where there has been considerable research recently. It should be appreciated that most literature reports on this subject do not define materials precisely, and therefore only an approximate idea of formulations can be offered here.

6.1.2 The Machine Tool

The following descriptions have some generality; they are not unique to GRP equipment.)

Conventional machining equipment consists essentially of a machine tool and a cutting medium. The important characteristics of the machine tool are its electric motor power, the quality of its bearings and its rigidity. This can affect cutting tool life or even prevent the use of hard but brittle diamond cutting tools.

6.1.3 Cutting Tool Materials

Plastics tend to have extremely abrasive properties, even though they do not necessarily need high cutting forces. Tool wear is proportional to the linear distance the tool travels in intimate contact with the material being cut. Conventional high speed steel tools are of little value when machining reinforced plastics laminates; the most widely used materials for cutting are tungsten carbide and diamond, because of their long tool life (i.e. interval between successive grinding operations).

Tungsten carbide is used in the form of finely divided particles, held together in a binder of cobalt, with or without additional carbides of titanium, tantalum, niobium or vanadium. The cobalt provides the softer

and more ductile support matrix and coating, while the hardness of the tungsten itself provides superior wear resistance. The grain size of the carbide is important, and can vary from sub-micrometre to five- or six-micrometre size.¹ The tungsten carbide tool is actually in the form of a tip, supported or clamped in a tool-post by a tool-shank or body (Fig. 6.1) and is often used in 'throwaway' form, to avoid the expense of regrinding.

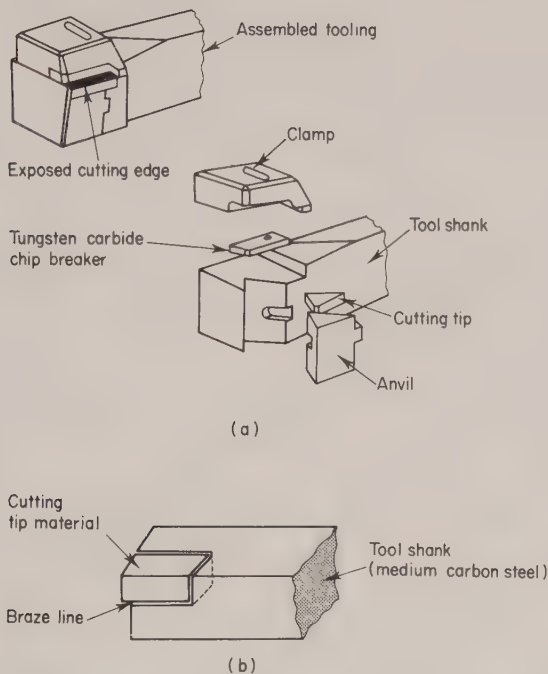


FIG. 6.1 Basic forms of carbide tooling for single point cutting. (a) Modular 'throwaway' tip cutting tool system. (b) Typical brazed tip cutting tool.

Various systems have been developed to assist the user in selecting the best grade of carbide for a specific application. Mention should be made of the British Standard, BS 4193, 1980² and of the British Hard Metal Association (BHMA) classification system.³ There are others, but according to Brookes⁴ only an approximate correlation can be made between the grade assignments of different manufacturers, which are

made on a qualitative basis. The ISO 513 uses an application code designated by one letter, followed by two digits, indicating the changing hardness and toughness of the carbide over a range of 19 basic codes. For example, a manufacturer might recommend ISO K40 or K10 for GRP or for certain phenolic laminates.

The BHMA designation is a three-digit system, the first digit indicating hardness, the second indicating transverse rupture strength and the third denoting the volume of added crater-resistant carbide.

So, if heavy wear is a problem, a higher-value first-digit carbide should be tried in order to alleviate the problem. The BHMA recommendation for highly abrasive materials would be 8-2-0.

Diamond is expensive, but it is also the hardest of the materials used in cutting. The economic application of diamonds for cutting has to be justified in specific instances.

Natural diamond has been used for many years, primarily for metallic materials, e.g. finish turning of automotive pistons. Since 1974, synthetic diamonds have been available in the United States. One early application of synthetic diamonds in GRP machining was in the turning of a 75% glass fibre epoxy composite.⁵

Some idea of the durability of diamond can be gained from the fact that during the machining of a fused silica valve cap, a carbide cutting tool completed four parts while the synthetic diamond tool completed 800.

Fabrication of polycrystalline (synthetic diamond) compacted tools is similar to that used for the brazed shank tungsten carbides. The diamond is supplied in the form of a disc,⁶ 8.4-13.7 mm in diameter, with a surface layer of sintered diamond powder bonded to a cemented tungsten carbide substrate. Polycrystalline tools do not possess the same hardness as the single crystal natural diamond, but because of its homogeneity and isotropic nature, a polycrystalline compact wears uniformly by micro-chipping of the cutting edge, instead of suffering a major fracture along cleavage planes as is the case with single crystal natural diamonds. Scriven⁷ discusses in detail the fabrication and uses of polycrystalline tools, with special reference to the machining of GRP. He also identifies the economic advantages and disadvantages of polycrystalline and carbide tooling. Since the diamond tool costs at least 50 times as much, it cannot always be justified simply on economic grounds, except for the reduction in reject rates, the greater consistency over long periods, and the improved surface finish of components. Scriven mentions the machining of a 2.3 m diameter GRP pipe, 10 m long, with a tooling set-up using

22 polycrystalline tools, which completed 150 pipes. A comparable set of much cheaper carbide tools did not complete a single pipe.

A more recent development by a large international diamond group⁸ has been the introduction of a synthetic diamond which is an extremely tough, intergrown mass of randomly oriented diamond particles in a metal matrix. Tool blanks are produced consisting of a thin layer of diamond bonded to a tungsten carbide substrate, which provides a support for the hard cutting edge. Bex and Roberts⁹ reported a significant improvement in performance when the rake face, i.e. the cutting face in contact with the sheared GRP, is finish ground and polished. This is done to reduce the coefficient of friction between tool and workpiece; an illustration is shown in Fig. 6.2, taken from the machining of a silica filled epoxy resin.

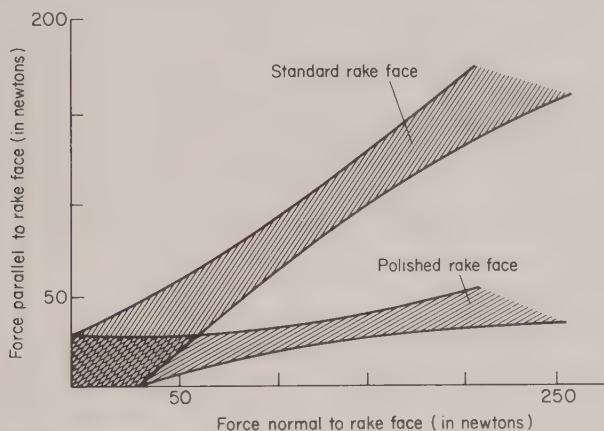


FIG. 6.2 90% Confidence bands for coefficient of friction (μ) — Grade 010 syndite cutting silica flour filled epoxy resin. (After Bex and Roberts⁹).

Tool life equations have been developed by a leading diamond producer;¹⁰ the form given below is based on the concept of equivalent chip thickness, h , a function which incorporates critical tool factors and machining variables:

$$T^a V h_e = C$$

where T = tool life in minutes, V = cutting speed in m/min, C and a = constants and h_e , the equivalent chip thickness, is in mm/revolution, defined in this case as the ratio: area of cut/length of tool edge contacting the work.

6.2 MACHINING TECHNIQUES

6.2.1 Cutting and Sawing

There are several literature sources of information on general machining techniques, notably Martin¹¹ and others.^{12,13} Martin makes specific recommendations for steel and carbide tipped circular saws for thermo-setting laminates. He draws attention to the existence of different machining characteristics for different resin systems; an epoxy-based printed circuit board laminate system of NEMA Grade 10 softens more readily at elevated temperatures than the other NEMA grades.

Shemilt¹⁴ discusses the roller cutter method of edge shearing for GRP laminates. The cutters, i.e. knives, will operate virtually without air cooling, resulting in a smooth cut, which is often the desired objective.

The sub-dividing or cutting up of laminate sheets is a major task, which can be an uneconomic operation both from the labour and materials standpoints. The materials loss is illustrated by the experience of a US manufacturer of quality PCBs using manual lay-outs,¹⁵ who reported a loss of 9% of his annual output of 850 000 ft² (91 496 m²) of material which at that time was valued at \$100 000. Changing to computer-generated cutting patterns is claimed to have reduced the scrap loss to an average of 3%.

6.2.2 Grinding

Juchem and Wapler¹⁶ discuss the grinding of both ceramic and GRP materials. Electroplated diamond tools using natural diamond grit types are preferred for GRP because these types are irregular, with rough surfaces, which permit good keying in the wheel bond to give a maximum grit-holding capability. However, synthetic diamond is preferred in cases where vibration is anticipated.

One special-purpose laminate cut-off saw manufacturer originally used an 85/100 mesh diamond saw, but has found that modern laminates, made from new resin formulations containing novel additives such as fire-retardants, require a 60/85 mesh.

6.2.3 Water-jet Cutting

When consideration is given to unconventional cutting techniques, it will be apparent that the electrical techniques used for difficult metals cannot be used with GRP since it is non-conducting. On the other hand, water-jet cutting has several advantages. The water jets use a pressure in the

range 40 000–60 000 psi (275–414 MPa) and will cut plastics and GRP with minimum loss of material from the kerf, and negligible heat generation—hence avoiding the degradation or melting sometimes found when cutting polymers by other methods. The usefulness of this technique is illustrated by its application to the machining of an asbestos material¹⁸ using machining procedures which completely satisfied OSHA health and safety requirements. Conventional methods were unacceptable, even with complete enclosure of machine tools. The machining was carried out with a numerically controlled machine tool, adapted to carry a 0.006-in (0.152-mm) diameter nozzle and the auxiliary equipment. The cutting of profiles was accomplished within a tolerance of ± 0.008 in (0.20 mm) between the line picked up by the photo-trace and the actual workpiece. The range of materials cut by the water jet includes cast acrylic sheet (polymethyl methacrylate), 9.5-mm GRP sheet and even a 0.5-mm boron fibre composite with added stainless steel wire reinforcement.

6.2.4 Laser Applications

Desforges¹⁹ identified six engineering applications of lasers, namely: cutting, drilling, welding, surface hardening, surface alloying and shock hardening. Of these, only the first two lie within the scope of this chapter. Cutting and drilling require the laser to operate in different modes—continuous and pulsed, respectively. For cutting, the limiting factor is the energy absorbed by the material. A 12.5-mm epoxy-glass laminate requires 20 kW for a cutting speed of 4.5 m/min, while a boron-epoxy sheet, about 9 mm thick, achieved a cutting rate of only 1.5 m/min at 15 kW.

Laser machining has the great advantage of being a non-contacting method, in that it involves no cutting forces and hence no tool wear. Within given power constraints the laser will cut diamond, fully hardened tool steel, GRP, and a range of other materials. Its precise profiling capability, narrow kerf and smooth cut edge are especially useful for GRP.

With pulsed laser systems, power densities are of the order of 10^8 W/cm². This high power density facilitates the machining of materials with high surface reflectivity, notably metals. It also helps with the removal of material debris. Short pulses can be advantageous in avoiding degradation.

A beam splitting device has been developed, which can operate two work stations with one laser, increasing the rate of hole drilling.

Production rates of 600 holes/min, for hole diameters from 0.1 to 1.0 mm, have been achieved, with tolerances of ± 0.0035 mm.

A laser manufacturer has suggested²⁰ that the working life of a laser system should be about 10 years, with an efficiency of up to 95%. Initial cost is a significant factor; the same source quoted £70 000 (in 1979) for a turnkey ceramic scribing laser.

Nevertheless, very high drilling speeds have been claimed for plastics, though hole quality, accuracy and layout details are not always given.²¹

6.2.5 Machining 'Advanced' Composites and Sandwich Materials

Many advanced composite materials are now available, particularly in the aerospace industry, which have a sandwich structure. These usually consist of outer skins of laminate enclosing a lightweight polymeric or metallic honeycomb core. The drilling of materials of this kind may require more than one type of drill. One US manufacturer had to resort to using up to five different drills to produce a 0.250 in (6.35 mm) diameter hole in a boron-epoxy skinned, titanium sandwich material. In this case,^{22,23} the problem of filament break-out was minimised by using a back-up material of phenolic or epoxy behind the composite structure.

Several unconventional approaches have been tried for drilling and trimming this kind of material. Among these are the use of a carbon-dioxide-assisted laser, electrochemical grinding and ultrasonic machining.

6.2.6 Safety Aspects

Reinforced plastics materials produce considerable fine dust when being machined. This can be abrasive to machine tools, bearings, etc., and can be a source of irritation and a health hazard to humans. Dermatitis,²⁴ lung irritation and explosion from resin dusts are among the main problems. Many countries have health and safety requirements which include demands for efficient dust collection. These requirements are likely to become more stringent.

6.3 POLYMERIC MACHINING ANALYSIS

6.3.1 Basic Concepts

Figure 6.3 shows the two-force cutting system which metal-cutting researchers, and subsequently a small number of polymer machining workers, have used for an analysis of cutting forces. Most practical

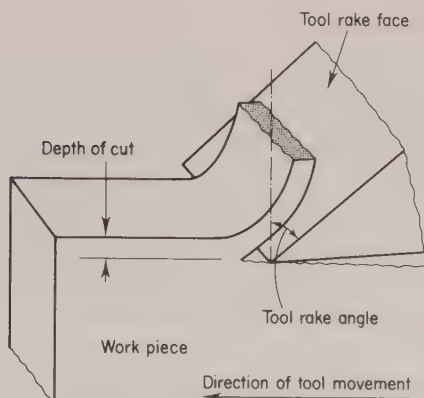


FIG. 6.3 Diagram showing an orthogonal cutting system.

cutting requires a three-force system, a procedure called oblique cutting, but this leads to considerable complication in any analysis.

6.3.2 Polymers and Reinforced Plastics

Kobayashi²⁵ published the first major contribution to the application of metal cutting theory to polymers. He observed that, for a given depth of cut and cutting speed, there existed a rake angle, at which the thrust force was always zero for a specific polymer. This finding was verified and extended by Young and Wilson²⁶ using polymethylmethacrylate (PMMA) and polyvinyl chloride (PVC). Rao *et al.*²⁷ studied the differences between chip formation in acetal, i.e. polyformaldehyde, and in polyamide (nylon). He noted the need to use small rake angles with acetal, in order to avoid a poor surface finish.

6.4 MACHINING ECONOMICS

6.4.1 Introduction

There is little information in the literature at present applying specifically to reinforced plastics. Boothroyd²⁸ and others have discussed in some detail the main factors affecting the economics of optimum cutting speeds for metals; these are illustrated in Fig. 6.4. One of the less obvious factors to consider is that cutting speed selection can be for minimum overall cost or for maximum tool life.

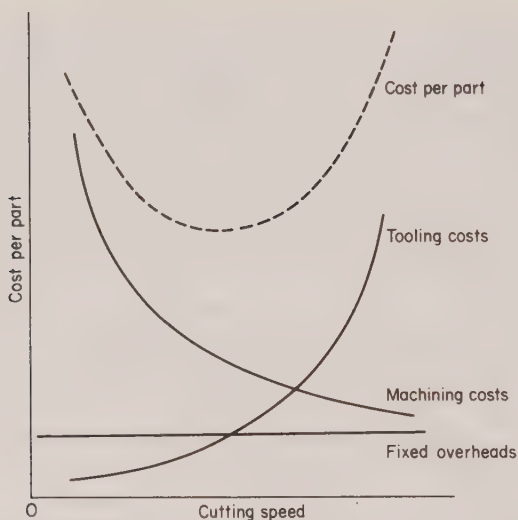


FIG. 6.4 General machining. Economic relationships for batch production of parts.

6.4.2 'Throwaway' Tip Tooling

The use of 'throwaway' tool tips has already been mentioned. Christ²⁹ and others have considered the effect on the economics of machining, and on the optimising of production rates, produced by not having to regrind tools and reset them. They deduced the relationship given below:

$$V = C / \left[\left(\frac{1}{n} - 1 \right) (T) \right]^n$$

where V = cutting speed for maximum production rate, C = the constant from the tool life equation in Section 6.1.3, T = tool change time and n = the tool material constant.

Once sufficient machining information is available for reinforced plastics, a similar relationship could be deduced and the data optimised by computer.^{30, 31}

One or two areas of GRP machining economics have already received detailed study. One of these will be considered in the next section.

6.4.3 Economics of Hole Production in PCB Laminates (see also Chapter 7)

The production of holes in PCBs can be carried out either by punching or drilling. Common PCB materials include paper-based phenolic, glass-epoxy, melamine, polyester and silicone laminates. Drilling is the technique used for the majority of 'professional' quality PCBs, partly because of the economics of small batch operations, but also because of consumer specifications, which tend to be tighter than those applying to the large scale consumer market. Generally, a comparison between the two hole production methods can be made by means of the equation

$$N = \frac{10H}{L_d(H/H_d - L_p/H_p)}$$

where N = number of parts per year, H_d = number of holes drilled per minute, H_p = number of holes punched per minute, L_d , L_p = labour cost per minute drilling/punching and H = number of holes per part.

This equation identifies the break-even point, N , between punching and drilling for PCBs having 100–500 holes/ft² (929–4645 holes/m²).

It will be apparent that batch quantities and frequency are the main factors determining the mode of hole production in any specific instance. For the very large mass market consumer applications, punching all the holes in one or two operations is economically essential; if the quantities of boards are large enough, the higher capital cost of the die-set will be justified. Golensbe³² estimates the economic scale at 40 000–60 000 holes per day per die-set. The number of holes punched per pass would usually be limited only by the press load capacity, the geometry of the individual hole patterns and the press-tool making facilities available.

Mehta³³ considered the merits of punching flexible laminates, rather than drilling, and the factors of importance are listed in Table 6.1.

6.5 THE DRILLING PROCESS

6.5.1 Introduction

The largest volume of GRP machining is in PCB manufacture³⁴ for which hole and edge profile manufacture are prime requirements. Weng³⁵ cites the chief advantages of drilling as: stable hole quality, reduced burr formation and the ability to produce holes of very small diameter in regular production (as low as 0.6 mm diameter).

TABLE 6.1

FACTORS AFFECTING THE ECONOMICS OF PUNCHING AND DRILLING HOLES IN LAMINATES FOR PCB PRODUCTION

1. Equipment costs	
<i>Drilling</i>	<i>Punching</i>
Drilling machine costs (high)	Punching press costs (low)
Tooling per product design (low)	Punch tooling (high)
Tooling per part: Drill bit back-up	Sharpening cost (low)
2. Manufacturing costs.	
<i>Drilling</i>	<i>Punching</i>
Pre-punching or pre-drilling of locating holes	No equivalent
Materials handling (manual)	Materials handling could be automated
Drilling rate 100 holes/min	Punching rate up to 50 parts/min
Inspection cost: Positioning accuracy check needed per part or lot	Per tool only

6.5.2 Drilling Machine Developments³⁶

Specially designed numerically controlled machine tools have been developed, often with multiple spindles (three or four), providing faster coordinate positioning and a very short, fast stroking spindle head movement (the total laminate thickness drilled rarely exceeds 8 mm). Icough³⁷ identifies 'high feed drilling' as the significant development in modern numerically controlled PCB drilling machines; this technique utilises chip loads well in excess of 0.038 mm/rev feed rate; thus, the typical three-board set-up of about 6 mm thickness requires about 160 revolutions at the standard feed rate (chip load) of 0.038 mm/rev, while 46 would be required at 0.13 mm/rev. Such a technique reduces both the production time and the heat generated while the drill is in contact with the reinforced plastics material. The new drilling/routing machine tool has recently become increasingly popular³⁷ as an economic way of meeting increasing demand for small batches of PCBs with a quick delivery service.

Al-Anbuji and Swadi³⁸ incorporated component-oriented subroutines in the software of an experimental microcomputer-controlled drilling machine. This was claimed to reduce the programming effort required considerably, and to reduce the human errors in writing the numerical control (NC) program.

A computer-aided design (CAD) system is described by Stureson.³⁹ The hole drilling data (or program) are generated in the form of an NC tape file at the stage when the master circuit board is laid out. Stureson mentions drilling rates of 12 holes/s for double-sided epoxy PCBs.

Some modern PCB NC drilling machines have automatic drill changing facilities, in which the number of holes produced by the drill is recorded in the control program of the machine—this facility reduces tool change time, avoids poor hole quality because of drill wear and increases the capital cost involved.

6.5.3 Drilling Analysis and Development

Kasmouski⁴⁰ lists limits for chip loading factors in the PCB drilling process as follows:

- (1) the volume of the drill flute.
- (2) the torsional strength of the drill.
- (3) the dynamic stability of the drilling machine.
- (4) the strength of the epoxy/copper bond (where applicable) in the PCB.

Both Kasmouski⁴⁰ and Arnold and Friedi⁴¹ emphasise the importance of optimising drill relief angle in obtaining maximum chip load for high feed drilling techniques. In practical geometric terms, this means that the limiting clearance angle is the rate of feed angle or the drill heel dragging effect. Arnold also examined in detail the configurations of a 'four-facet' drill point. He suggested that for inspection of carbide PCB drills of less than 2 mm diameter, a stereo-microscope with 30–50× enlargement should be used to ensure sufficient accuracy when checking drill cutting geometry.

Kobayashi's initial work on drilling of thermosetting and thermoplastic materials⁴² showed an interesting variation in both drill torque and thrust forces between the two materials during the drilling of deep (30 mm) holes. He also studied drill wear during the drilling of GRP and found that the thrust force increases rapidly, while the drill torque does not increase significantly.

The effects of GRP laminates on drill performance have been examined by Weiss.^{43,44} Firstly, he was concerned with the problem of 'epoxy

smear' (a nail heading of the epoxy layer within a PCB multilayer board). Weiss determined that drill temperature and drill life were the significant factors and hence studied the problem of drill wear by means of a drill monitoring system. Secondly, he related drilled hole quality to the energy required to drill the hole. He discovered that a higher drill life could be obtained using a higher feed rate or chip loading than with a lower feed rate and the same volume of work done.

Kobayashi and Tsukada⁴⁵ studied the performance of commercial grades of carbide drills in relation to hole quality, initial drill geometry, drill wear patterns and other drilling parameters. They subsequently developed from their researches a new plated drill, claimed to have better chip removal because of the low frictional resistance of the chip against the plated surface. This was also said to eliminate epoxy smear because of lower heat generation. They concluded that optimum drill speed and feed rate were vital in order to achieve surface roughness close to $5\text{ }\mu\text{m}$ and dimensional accuracy close to $10\text{ }\mu\text{m}$.

Hagge⁴⁶ investigated the drilling of PTFE/glass laminates. This material gave problems deriving from lack of adhesion between polymer and fibres, resulting in exposure of the fibre bundles; hence sharp drill bits were required in order to be effective in producing a hole side-wall contour of the appropriate quality. Increasing the feed rate was found to eliminate PTFE smear—this was partly caused by clogging within the drill flute. The same drill specifications used for PTFE boards could be used for epoxy ones.

6.6 THE PUNCHING PROCESS

6.6.1 Power Press Design

In the lower punching capacity press range, the 'C' frame design predominates because of the relatively low capital cost of the machine and its fast crank speed of working; hence a large volume of PCB production is carried out on this type of machine (see Fig. 6.5). The 'open throat' design offers maximum access and ease of operation for high production rates, both with automatic and semi-automatic operation.

The alternative machine design, generally used for large capacity working, has an enclosed, box-like structural design which is also shown in Fig. 6.5. This is intended for heavier punching loads. The machines are often geared down to a slower shearing speed, both for dynamic and economic reasons. In the PCB industry, these heavier capacity presses

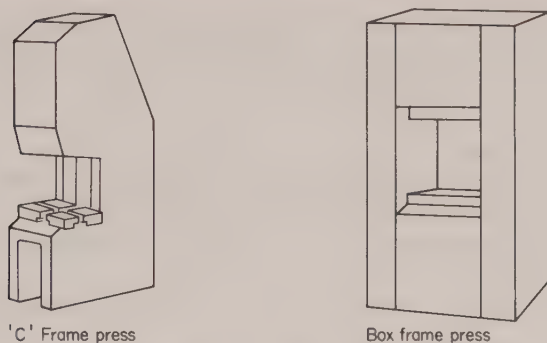


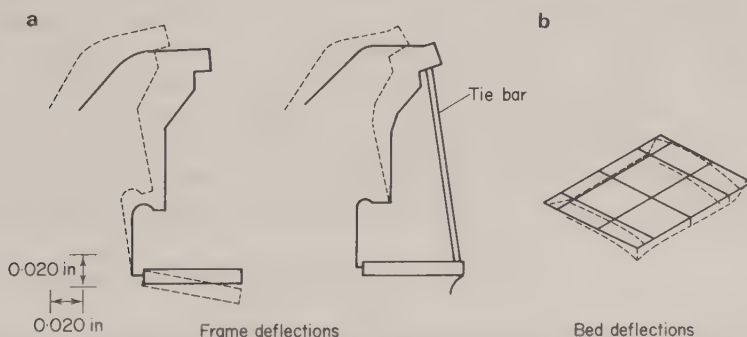
FIG. 6.5 Basic designs of pressworking machine-tools.

are used more frequently for multiple board working, in which the number of boards punched simultaneously is arranged to suit the normal press working area or the load capacity of the machines.

Such methods of working are found chiefly in those commercial markets where high expenditure on machines and tooling would be economically justified. The important feature of the box structure is that it avoids the machine frame deflections associated with the lighter type of press and its open cantilever design.

6.6.2 Power Press Dynamics

Studies have been made of the static and dynamic characteristics of the 'C' frame press mentioned previously.⁴⁷ The effects of a full rated capacity load applied along the centre line of the machine-tool under test produced the movement shown in Fig. 6.6a. The effect on the machine-

FIG. 6.6 Deflected shapes of press frame (a) and bed (b). (After PERA⁴⁷).

bed is shown in Fig. 6.6b. Considerable elastic deformation takes place, which can be reduced significantly if the press is fitted with tie-bars. Reductions of 45% have been achieved.

6.6.3 Tool-set Design

While the machine structural design allows some inherent deflections which affect the alignment of the working axis, so the tool-set geometry and design can restrain or restrict the errors introduced by the actual punch and die action.

Selection of the punch set is made with due consideration for the following:

- (1) The size of work area required.
- (2) The press capacity (with reference to tooling).
- (3) The precision required.
- (4) The total number of parts required.

The cheapest tool-set design would merely provide the minimum location and alignment between punch and die. This generally consists of two accurately produced location pins, provided with the minimum of diametral clearance to sustain an accurate alignment during the short press stroke. Such techniques are limited by the skill of the tool maker as well as by price considerations and, inevitably, the accuracy can be maintained for only a short life. Even then, reasonable care and maintenance has to be taken to achieve the minimum acceptable economic tool life.

Several companies offer a wide range of different sizes of a basic modular die set, with a form of enclosed pillar alignment, consisting of a standard rotating captive ball-bearing sleeve or a simple bearing. The sets are available in two- or four-pillar designs, to facilitate an additional accuracy of location when increased precision or size of working is necessary. The tool life of this basic unit of the tool-set far exceeds the cutting-tool life of the actual punches and dies used, and being of modular construction, the unit can take accurate relocations and replacements where necessary. The ready commercial availability of these sets with enclosed pillar guidance provides extensive tool life at an overall cost which would not be easily approached by an 'in house' tool-making facility.

6.6.4 Tool-set Dynamics

The effect of press frame elasticity on punch kinematics has been reported.⁴⁸ The detrimental effects of frame deformation were clearly

shown together with the added effect of slideway clearances on horizontal punch movement under simulated blanking conditions. No conclusions were drawn about punch and die guidance and/or the effect of the tool-set on the accuracy of the component. However, it would seem that at full or nearly full rated load capacity, the deflections and movements inherent in the press configuration can best be minimised by the use of tie-bars and die-sets with caged ball-bearing guides—particularly on account of the horizontal side thrusts from the ram and drive. These detrimental effects are exacerbated still further if the punching forces are not in axial alignment with the press axis; that is, if the component blank has a non-symmetrical lay-out of holes and/or contour.

Hojo⁴⁹ used a range of tool sets and recommended that sharp corner tools should be provided with a small radius to avoid the adverse effects of a notch and its propensity to cause crack propagation. He also studied the problem of punching small-diameter holes, and found that the lifting of the laminations of the phenolic-paper board was indirectly proportional to the punch clearance, but this problem was not noticed in holes of more than 6 mm diameter. Hojo suppressed crack formation by using alternate applications of opposing punches, and also imposed a side force on the blank to suppress microcracks.

A development announced by the Tokyo Print Company⁵⁰ consisted of a tool design change intended to assist in swaging the copper foil into the mouth of the punched hole, and hence form a much stronger meniscus when flow soldered.

Turret presses carry a range of different punches stored in a carousel. They offer an economic answer to the problems of small batch manufacturing, but the noise emanating from these presses can be very high, and one leading manufacturer has introduced a 'whisper punch' tooling modification⁵¹ which reduces the contact noise in metal working by about 12 dB. This tooling incorporates a punch face angle of between 3° and 10°, ground onto the piercing and blanking tools. A turret press is available with a combination of laser and mechanical working, so that the laser can be used for intricate contours and very large cut-outs which exceed the maximum punching diameter and load available at the press.

6.6.5 Analysis of the Shearing Process

6.6.5.1 The Shear Crack Mechanism in the Punching Process

The punching process is essentially a high speed shearing process, and

Fig. 6.7 (from ref. 52) shows the forces acting on a part-sheared section. Both Hojo⁵² and Frerichmann⁵³ studied the process by using the technique of partial punch penetration of the sheared zone in their paper-phenolic specimens; both used an instrumented press rig to record punch load characteristics. As well as paper-phenolic materials, Frerichmann studied a wide range of thermoplastics including polyethylene, polystyrene and rigid PVC.

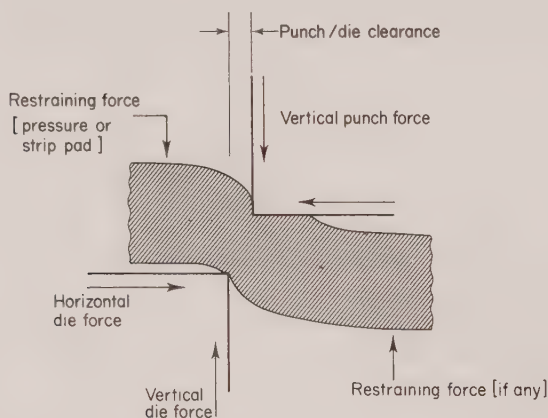


FIG. 6.7 Forces acting on part-sheared section. (After Hojo.⁵²).

Both workers identified the micro and macro crack formation characterising the phenolic-paper laminate materials. Hojo defined four stages of cracking in the shearing process:

- (1) Initial sheet flattening.
- (2) Elastic deformation.
- (3) Fine cracking (also called microcracking) within the material, accompanied by inter-laminar movement.
- (4) Secondary cracking. Primary shear occurs along the line of punching. Then punch force falls rapidly.

Hojo noted that the sheared-edge profile of paper-based phenolic laminates is similar to that obtained when shearing ductile sheet metal.

Figure 6.8 shows the stages of shearing identified by Hojo. He noted that numerous micro cracks remain in the sheared zone, and that the broken band is composed of a combined micro and macro cracked surface. The formation of very small holes was by a modified mechanism.

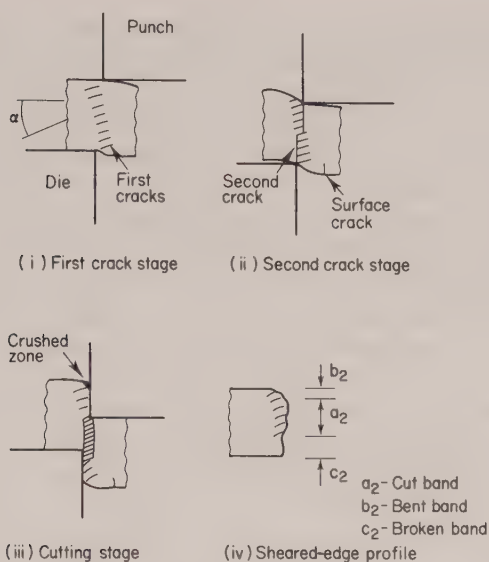


FIG. 6.8 Stages of shearing and sheared-edge profile. (After Hojo.⁵²).

Secondary cracking was dependent on punching conditions, such as the restriction applied and the degree of heating, but the initial fine cracking was scarcely affected by punching conditions.

6.6.5.2 Shearing Forces in the Punching Process

Hojo related his shear crack mechanism to the punch load v. punch penetration diagram obtained from his instrumented die-set. The total penetration was found to be 15–25% of sheet thickness before fracture of the blank was completed. The punch load clearance curve did not appear to have the same form as that obtained from Chang and Swift's experiments with metals.⁵⁴

It is often necessary to pre-heat laminate material prior to punching. Frerichmann gives some details of this, citing temperatures of 130–140°C for paper-phenolic laminates, with a heating time of 10–20 min.⁵³ Learmonth and Watson⁵⁵ also studied optimum heating procedures and examined the effect of cooling time on laminate punching quality. They utilised a stress-strain plot derived from the punch load diagram; their stress definition was that for the engineers' shear stress, while strain was defined as punch penetration, expressed as a percentage of nominal sheet thickness. These stress-strain diagrams could be divided into five main

regions, apparent at ambient punching temperatures only. It was suggested that these regions could be correlated with Hojo's stages of cracking.

The same authors used the parameters 'strain at break' and 'time to break'⁵⁶ as criteria for analysis of laminate performance, but since both these functions are derived from the same source, i.e. the punch load v. time data, they give results of very similar form.

Pritchard⁵⁷ used both punch load and shear energy as criteria for punching quality of both GRP and paper-phenolic laminates, using an instrumented commercial die-set to indicate punch loads and displacements. The most important factor deciding the punch energy was found to be the surface density of glass mat used, together with punching temperature.

Figure 6.9 summarises the punching behaviour of a series of polyester-glass laminates. The glass reinforcements included glass felt, various woven fabrics and continuous swirl mat.

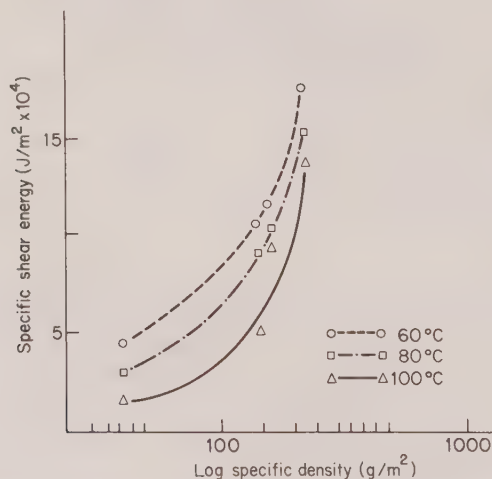


FIG. 6.9 Relationship between logarithmic surface density of reinforcement and specific shear energy for a range of punching temperatures.

6.6.5.3 Punch Stripping (Jump-up) Forces

The removal of the punch laminate from the punching tool is normally achieved by designing a stripping-plate or stripping-pad into the tool-set. Hojo used a strain-gauged type of dynamometer in one of his five different tooling set-ups⁵² and found that the stripping force was directly proportional to punch and die clearance above 3%.

The specific stripping force was given by the product of the coefficient of friction of the blank on the punch, μ , and the normal pressure. It was found that μ varied between 0.3 and 0.5, and if the specific stripping force became too high, the laminate would fracture or crack as a result—not because of the punching forces. The stripping operation is obviously of considerable importance in industrial practice, both in regard to the magnitude of the forces involved and the consistency with which the operation is achieved. Brobryn⁵⁸ found the stripping load during cold punching of paper-phenolics to be about 10–12% of the maximum punch force. This can be compared with observations⁵⁹ that the value of the stripping force in the punching of medium and high carbon steels never exceeds 10% of the punch force, but depends on the tool geometry.

Figure 6.10 shows the significant effect of punch stripping forces in hot punching operations, reported by Pritchard,⁵⁷ using a strain-gauged stripping-pad with an instrumented tool-set. If the total stripping load required to remove a laminate exceeded the stored energy available from the Belville washer normally used, it was found that heating the laminate by 40°C could reduce the stripping load by 50%.

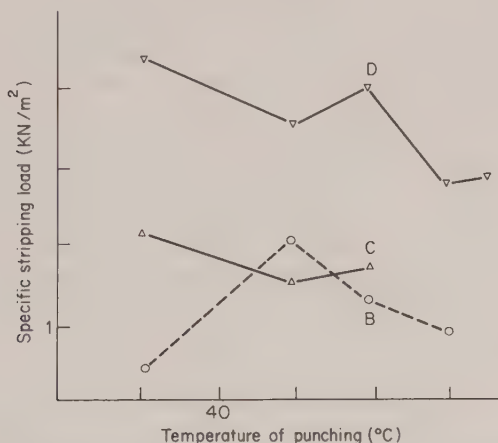


FIG. 6.10 Variation of specific stripping load and temperature of punching for commercial phenolic laminates. B, hot punching; C, hot punching-oil modified; D, hot punching-high resin content.

6.6.6 Assessing the Punchability of PCB Laminates

Ideally, the criteria for assessing the punchability of laminates should be objective rather than subjective,⁶⁰ but this eliminates all the methods

currently employed by the material manufacturers. Several methods have been proposed, including an ASTM (D 617) in which defects are compared with standard photographs. Radovsky⁶¹ and Nankano⁶² both produced oscillograms from a strain-gauged punch set-up. Comparatively simple tests include DIN 53488, which merely indicates resistance to cracking, and the Phillips penetration test,^{63,64} in which a small-diameter punch is applied by a cantilevered weight and the time of penetration is taken as the criterion. This is an on-line procedure suitable for PCB manufacturers.

6.7 MACHINABILITY INDICES

Machinability indices are widely used in production engineering applications, such as process planning, and in some NC computer-aided part programming languages. The metal cutting index is usually related to the cutting speeds recommended for commonly machined materials such as mild steel. Other metals can be related to mild steel. In the case of composite materials, there is not yet a sufficient breadth of experience among skilled workers to build up the necessary data-bank. With increasing use of reinforced plastics, the opportunity is arising to build up a store of data on the machining of the commonest kinds of FRP, i.e. paper-based phenolics, glass-epoxy laminates, glass-polyester laminates, etc. The problem is complicated by the considerable variety of form of the various materials; for, although most of the resins are more or less brittle at room temperature, they often contain fillers or flexibilisers, and the reinforcement can take many forms with various orientations. At present there is simply not sufficient information to generalise about the machinability of composites.

6.8 CONCLUSIONS

Current techniques for machining reinforced plastics rely heavily on carbides and on diamond cutting tools, because of the extremely abrasive nature of glass reinforcement. Machining GRP can constitute a health problem unless suitable precautions are taken; jet-cutting offers certain advantages in this respect.

Hole manufacture by drilling or punching continues to represent the bulk of FRP machining work, and the requirements of microelectronics

are such that hole sizes are becoming smaller. 'High feed' NC drilling machines increase productivity and reduce heat generation while cutting the board. Computer-aided design is now an established methodology with most large-volume PCB producers.

A major problem in all FRP machining is the need for high cutting speeds and greater machine rigidity. A problem specific to PCB manufacture is the limitation placed by existing die-set designs on removal of large sheets of sheared laminate from the punches. This limits the number of piercings per die-set.

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Chapter 7

PRODUCTION AND PROPERTIES OF PAPER-BASED LAMINATES

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SUMMARY

The historical development of paper-based laminates is briefly outlined. Modern manufacturing methods are described and the relationship between materials used and ultimate laminate properties is discussed.

There are two main classes of paper-based laminate: decorative, and industrial (or electrical) grade materials. Their properties depend on the precise choice of materials and also on cure characteristics and fabrication methods. The study of resin cure by such methods as differential scanning calorimetry and by rheological methods is therefore important.

The properties required for the most important current commercial applications are discussed. Two specific improvements in recent years are (1) post-forming laminates and (2) laminates of improved scratch and wear resistance.

Probable future trends in paper-based laminate technology are set out, emphasis being on the probability of continued steady evolution rather than a dramatic change either in material usage or fabrication principles.

7.1 INTRODUCTION

A wide variety of products is described by the term 'paper-based laminates'. This ranges from thin films, consisting perhaps of two plies of

paper or paper-metal foils used in packaging, to thick boards used as decorative or electrical laminates in the construction and furniture industries or printed circuit board manufacture. Only the latter materials can be fairly described as reinforced plastics and therefore comprise the subject of this chapter.

Laminates prepared from synthetic phenol-formaldehyde resins with paper as a reinforcement represent the earliest of modern laminate or reinforced plastic materials. Synthetic phenolic resins were first developed by Baekeland in 1908.¹ In 1912, Baekeland was granted a patent² which claimed a product made by superimposing layers of paper combined with intermediate layers of an insoluble and infusible condensation product of phenols and formaldehyde. Phenol-formaldehyde resins alone are brittle, and the use of layers of paper or cotton fabric as reinforcement strengthened the resin and allowed the production of large sheets, tubes and rods of material which could be fabricated.³ The appearance of these early industrial laminates was not important. They were used for their properties of electrical insulation, mechanical strength and chemical resistance.

The development of decorative laminates began about 10 years after the first work upon industrial laminates. Cochrane⁴ coated printed papers with phenolic resins and used these as decorative surfaces upon paper-phenolic resin laminates. Although such laminates had good wear and scratch resistance properties, and were used for tabletops, their good appearance was limited, of course, by the dark colour and poor light resistance of phenolic resins. The development of urea-formaldehyde and melamine-formaldehyde resins, which were essentially colourless and did not yellow after exposure to light, greatly improved the potential appearance of decorative laminates. During the last 40 years, most decorative laminates have been produced from paper-reinforced melamine-formaldehyde surfaces, laminated to several plies of paper-reinforced phenol-formaldehyde resin. These laminates have been increasingly used for kitchen work surfaces, furniture and wall cladding. In 1977 the European production of decorative laminates was estimated at about 160 million m² (ref. 5), about 47% of which was used for kitchen or other domestic furniture.

In recent years, the main use of industrial paper-based laminates has been for the manufacture of printed circuit boards. Although other laminate materials have been developed, particularly those made from epoxide resins and woven glass with better electrical and water absorption characteristics, the growth in domestic electronic equipment

has maintained a large market area for the significantly cheaper paper-phenolic laminates. The original laminate is made from several plies of paper, impregnated with phenolic resin and one surface ply of copper foil. The circuit tracks are made by etching unwanted areas of the copper after application of an etch-resistant ink. Holes are punched into the laminate, the component wire inserted into the holes and the circuit tracks of the board coated in solder to protect the copper and to connect the component wires to them.

7.2 MANUFACTURE OF PAPER-REINFORCED LAMINATES

In the case of both decorative and industrial laminates, the method of production consists of two consecutive stages. Firstly, reels of paper are impregnated with a solution of thermosetting resin and most of the solvent removed by passing the web of impregnated paper through a series of ovens. Figure 7.1 shows the so-called 'wet end' of a treating machine. The web of paper is seen entering the machine, after which it passes through a bath of melamine-formaldehyde resin solution. The vertical area of the paper in the photograph has been impregnated and, on the extreme left of the photograph, the wet web can be seen entering the first of a series of ovens.

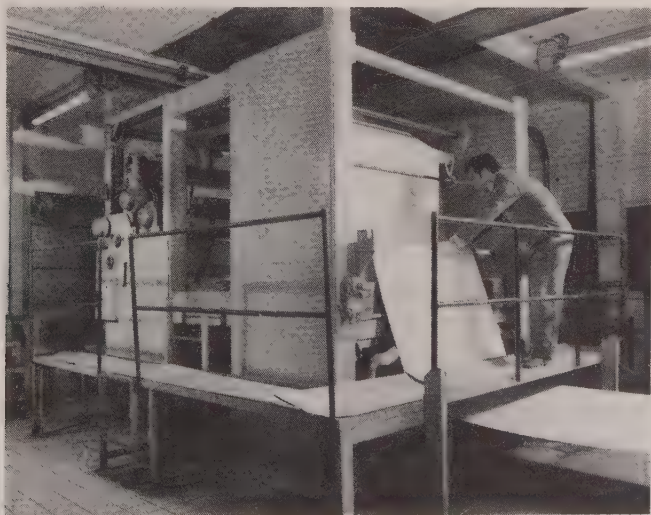


FIG. 7.1 The impregnation of surface paper with melamine-formaldehyde resin.

The second stage of the process for making a laminate involves pressing together plies of impregnated paper at elevated temperature. Typically, the pressure employed is about 100 kg/cm^2 or 10 MPa and the maximum temperature of the cycle between 130 and 150°C . Figure 7.2 shows the variation of temperature with time for a fairly typical lamination cycle.

The plies of impregnated paper are loaded into the press between stainless steel plates. The presses used to prepare decorative and industrial laminates are of the 'multi-daylight' type. In other words, the presses consist of a series of heated pairs of platens between each of which can be placed several assembled sheets of impregnated material contained between press plates. Figure 7.3 shows schematically a normal assembly between one pair of platens. In this case, two laminates are being pressed back to back with a release film as a separator. Typically, five or more such assemblies, and therefore 10 or more boards, would be pressed between each pair of heated platens.

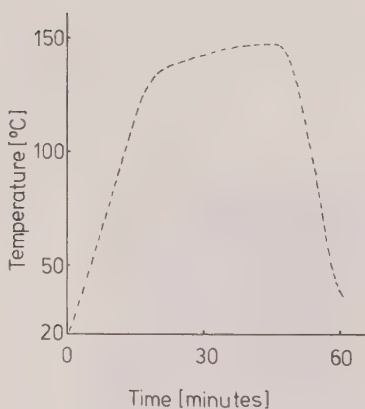


FIG. 7.2 Typical time-temperature profile for lamination.

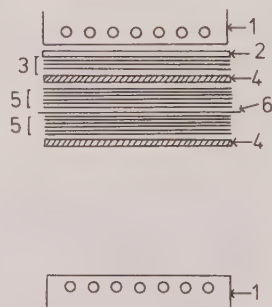


FIG. 7.3 Typical press assembly for production of a decorative laminate. 1, Heated platen; 2, soft iron plate; 3, pads to equalise pressure; 4, stainless steel plate; 5, impregnated papers and 6, release film.

Presses vary considerably in platen size and the number of pairs of platens. However, in a fairly normal press for decorative laminate production, there may be 24 platen openings (daylights) and each board may be $8' \times 4'$ ($2.44 \text{ m} \times 1.22 \text{ m}$). In each press load, assuming 10 boards per daylight, a total area of about 700 m^2 of decorative laminate would

be produced. Larger presses exist which can produce three or four times this area of laminate during a single cycle.

Decorative laminates are normally used as large sheets for kitchen work surfaces or wall coverings, whereas industrial laminates are usually employed in small areas as insulation boards or printed circuit boards. A wider variety of electrical laminates exists than is the case for decorative laminates, and batch sizes are therefore smaller. For all these reasons, presses for industrial laminates are often smaller than those used in decorative laminate production.

The basic method of making paper-based laminates has not changed since they were first developed. Improvements have been made in the size of presses, and in the degree of automatic control of press cycles and the impregnation process. It is normal, for example, to determine the level of resin in an impregnated web by means of β -gauges which scan both the treated and untreated web. The speed of web or the geometry of doctor blades or rollers in the treating head are then adjusted automatically by a control loop in order to achieve the required proportion of resin in the impregnated paper.

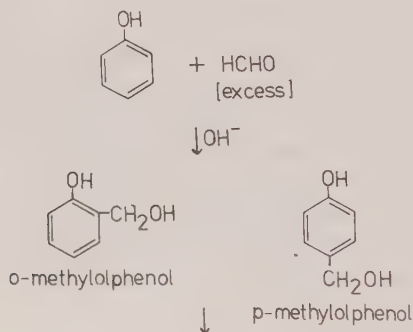
7.3 RAW MATERIALS

7.3.1 Resins

For the vast majority of paper laminates, the two main resins employed are of the phenol-formaldehyde or melamine-formaldehyde type. It is possible to use polyester resins based upon diallyl phthalate for the surfaces of decorative laminates and brominated epoxide resins are used to prepare some paper-based electrical laminates. However, the present discussion will be restricted to resins based upon phenolic or melamine nuclei.

Phenolic resins can be made by two different routes. The reaction between phenol and formaldehyde can be catalysed by base or alkali to produce a 'one-stage' resin, commonly known as a resole. On the other hand, the reaction may be catalysed by acid and with a low ratio of formaldehyde to phenol. The resin type produced by this means, known as novolac, can only be crosslinked to its final infusible state by mixing it with a compound capable of providing additional formaldehyde. Such a resin is therefore a 'two-stage' resin. Formaldehyde is most commonly provided by hexamethylenetetramine during the second, crosslinking stage.

The chemistry of phenol-formaldehyde resins is extremely complex, and only the principles will be discussed in this chapter. Several comprehensive textbooks upon the chemistry of phenolic resins have been published.⁶⁻⁸ The normal type of phenolic resin used in laminate manufacture is a resole. If phenol is reacted with formaldehyde in the presence of alkali, a mixture of phenol alcohols is produced. This is represented simply in Fig. 7.4.



Di- and Trimethylolphenols

FIG. 7.4 Initial reactions between phenol and formaldehyde under alkaline conditions.

Under such alkaline conditions the further reaction of methylolated species to produce higher molecular weight material is relatively slow. Resole resins used to impregnate laminating papers normally consist of a mixture of mono- and di-nuclear species, with a small proportion of higher molecular weight material.

During the lamination stage of preparing a paper-reinforced laminate, the phenol alcohols undergo condensation reactions to produce species of higher molecular weight, branched molecules and finally gels. The mechanisms of these reactions are not fully understood (see refs. 8 and 9 and references therein). However, the condensation reactions occurring between methylolated species can be represented by the general scheme shown in Fig. 7.5. The final crosslinked structure consists mainly of phenolic nuclei connected by methylene groups.

The molar ratio of formaldehyde to phenol used to prepare decorative laminates is in the range 1:1 to 2:1. Post-forming laminates, which are discussed more fully later, are normally prepared with resins having formaldehyde to phenol ratios at the lower end of this range.

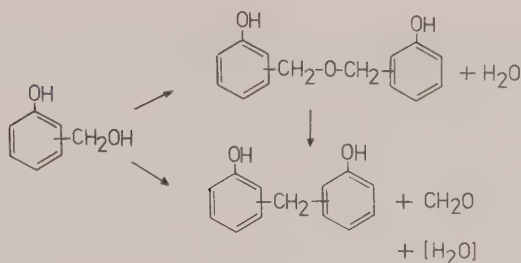


FIG. 7.5 General scheme for the condensation of phenol alcohols.

Phenolic resins for decorative laminates are sometimes prepared in the presence of ammonia or amines as catalysts. This can result in resins containing amine groups within the crosslinked structure.^{8,10} In the case of resins for electrical laminates, tertiary amines such as triethylamine are often used. It is important that the final laminate contains no charged species, hence ionic catalysts such as sodium hydroxide are normally avoided.

Laminates used for the production of printed circuit boards are often prepared from two phenolic resins. The first of these is a low molecular weight, low viscosity resin which can penetrate the cellulose fibres of the paper reinforcement. The second resin is often a more hydrophobic, modified resole resin of higher molecular weight, usually designed to be less brittle and therefore to have better punching properties than a normal phenolic resin. This will be discussed in more detail later.

Many of the basic principles of melamine-formaldehyde resin chemistry are similar to those for phenol-formaldehyde resins. Melamine (2,4,—triamino—s—triazine) reacts firstly with formaldehyde by an addition process, and then the methylolated species condense to produce higher molecular weight material and finally a crosslinked polymer. In the addition stage, which is normally performed under mildly alkaline conditions (pH 8–9.5), the electron-rich nitrogen atoms of the amine groups in the melamine molecule attack the electron-deficient carbonyl carbon atom of formaldehyde as shown in Fig. 7.6. There are, in principle, six sites at which methylolation may occur. At the ratios of formaldehyde to melamine normally used, a mixture of mono-, di- and tri-methylolmelamine is formed.

Under the alkaline conditions used to prepare the resin, and at room temperature, this mixture of methylolated species is relatively stable. Condensation takes place rapidly at elevated temperatures and is catalysed by acids. The general reaction scheme is shown in Fig. 7.7.

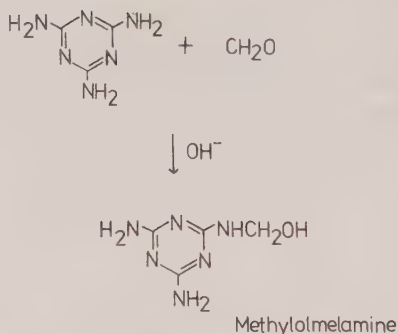


FIG. 7.6 Initial reaction between melamine and formaldehyde to produce methylolmelamine.

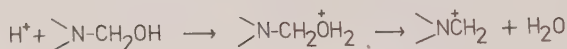


FIG. 7.7 General reaction scheme for the acid catalysed condensation of methylolated melamine species.

The final, three-dimensional, crosslinked structure therefore consists of triazine rings joined together by methylene groups shared between the amine nitrogen atoms of adjacent melamine nuclei.

Normally, the molar ratio of formaldehyde to melamine used to prepare resins for decorative laminates is in the range 1.5:1 to 2.5:1. The formulations of melamine resins for post-forming laminates can be rather different from these simple mixtures of melamine and formaldehyde and will be discussed in more detail in Section 5.

7.3.2 Papers

Most of the papers used to prepare electrical and decorative laminates are made from a softwood source using the Kraft or sulphate process. The wood, in the form of chips or sawdust, is digested in a mixture of sodium sulphide and sodium hydroxide. The lignin content of the wood is reduced to a level determined by the specific property requirements of the paper and the pulp may then be bleached before making the paper.

Several specific properties of papers are required depending upon whether they are to be used for decorative or electrical laminates and whether they are to be used for surface, print or core plies. In all cases, the paper has to be of fairly high porosity in order to be capable of absorbing a large proportion of resin. For economic reasons, it is often necessary that the paper can absorb a resin solution rapidly. Porosity is therefore normally measured for quality control purposes. The rate of passage of air through a sample sheet under standard conditions is one such measurement. This is carried out using a Gurley densometer. Alternatively, or additionally, the height to which water will travel by capillary action into a vertically held strip of paper after a certain time interval can be measured as in a Klemm absorbency test. More detailed information concerning the pore structure of paper can be obtained using the technique of mercury porosimetry. In this method mercury is forced into the pores of a paper sample by successive increases in pressure and the volume of mercury absorbed is measured. The pressure required to cause intrusion of the mercury is simply related to the size of the pore into which it enters. A distribution of total pore volume against pore radius can thereby be obtained.

For electrical laminates, used to prepare printed circuit boards, papers are normally bleached and contain low levels of ionic impurities. Surface papers are sometimes of greater quality than those used for interior plies, for which electrical properties are less critical. Such laminates can contain up to about 60% w/w resin, at least in their surface plies. Paper made from cotton linters is easier to impregnate with phenolic resin than is paper prepared from wood fibres. It also exhibits good punching and electrical properties. It is sometimes used for these reasons but is more expensive than paper made from wood.

Paper-based phenolic laminates are used for construction and for simple electrical devices which do not require the same high level of electrical resistance or the intricate processibility of printed circuit board laminates. They may also need to be of high mechanical strength. A range of industrial laminates is therefore available with different minimum mechanical and electrical properties. This range is defined by various national and international standards such as those specified by the National Electrical Manufacturers Association (NEMA).¹¹ In general, for products of higher mechanical strength and inferior electrical properties, less purified papers, impregnated at lower resin contents, are employed.

A decorative laminate has the general structure shown in Table 7.1:

TABLE 7.1
GENERALISED STRUCTURE OF A HIGH PRESSURE DECORATIVE LAMINATE

<i>Paper</i>	<i>No. of sheets</i>	<i>Substance weight (g/m²)</i>	<i>Resin type</i>	<i>Resin content (%w/w)</i>
Overlay	1	30-50	M/F	65-75
Print sheet	1	80-150	M/F	30-50
Core paper	Several	100-200	P/F	25-35

The overlay paper and print sheet are prepared from highly purified α -cellulose. The overlay paper has to be highly absorbent in order to retain the necessary proportion of melamine-formaldehyde resin. The refractive indices of cellulose fibres and melamine resins are 1.55 and 1.62 respectively, and this small difference causes some light scattering to occur. The thicker the overlay the lower the transparency and therefore the print clarity. However, an increase in thickness will also cause an improvement in the wear properties of the laminate. The chosen thickness of the overlay sheet represents a compromise between these opposing factors.

The print sheet has to have a relatively smooth surface for satisfactory printing. It also serves as an optical barrier to the dark colour of the phenolic resin core sheets. For this reason, it is normally filled with titanium dioxide at a level of 20-35% w/w and contains other pigments in order to achieve the required tone.

The core paper, often known as saturating kraft, does not need to be processed to the same degree of purity as the decorative surface layers, but the lignin content has to be reasonably low (5-8% w/w) in order to facilitate impregnation. There are many variations of the above type of laminate construction. Sometimes a thinner print sheet is used, with an extra ply of melamine-resin-impregnated opaque barrier sheet below. A barrier sheet of melamine-resin-impregnated bleached kraft paper is sometimes used between the print and core layers in order to avoid the problem of migration of the brown phenolic resin from the core to the print sheet during lamination.

7.4 FLOW AND CURE OF RESINS DURING LAMINATION

An understanding and control of the flow and cure properties of resins is essential in the production of paper-based laminates. From an economic

standpoint, the time and temperature profiles of press cycles have to be minimised. On the other hand, resins have to be properly crosslinked in order to achieve satisfactory properties, such as dimensional stability, under conditions of changing humidity, electrical insulation and heat or scratch resistance.

Too much resin flow can, in an extreme case, lead to wastage of resin during lamination and consequently a product of low resin content. Too little flow can give rise to exposed cellulose fibres which can act as channels for the transportation of water or, in the case of an overlay layer in a decorative laminate, a loss of transparency.

Resin flow is particularly important for decorative laminates. Wear resistance is dependent upon the retention of a satisfactory layer of melamine resin above the print sheet. The decorative appearance would be spoiled by migration of phenolic resin from the core sheets into the print sheet.

In production, the properties of resins and impregnated papers are controlled by simple tests. A sample of treated paper may be placed in a small press at a chosen temperature and for a certain interval of time. The flow of the resin can be observed and the cure of the resin can be checked by measuring the proportion which is soluble in hot water. The reactivity of a melamine resin solution can be determined by measuring the time taken for a sample to become milky at 100°C.

During the development of resins and the optimisation of press cycles, more-fundamental studies are usually made. The curing characteristics of melamine and phenolic resins can be studied by such techniques as torsional braid analysis, dynamic mechanical analysis and differential scanning calorimetry. For each of these methods, mathematical models can be employed which relate the state of cure to temperature and time.

Differential scanning calorimetry (DSC) is one of the more important techniques. The method involves the simultaneous heating, at a predetermined rate of temperature increase, of two cells. One contains the sample and the other is empty and acts as reference. The cells are always maintained at equal temperature and the difference in the rate of heat supply to them is measured. If the sample melts, the rate of heat flow to the sample increases to compensate for this endothermic transition. A trace of the rate of heat flow against temperature exhibits a peak which corresponds to this additional supply of heat.

In the case of resin cure, the crosslinking reactions are normally exothermic, and a peak is obtained representing the decrease in the rate of heat supply to the sample which therefore occurs. Figure 7.8 shows the

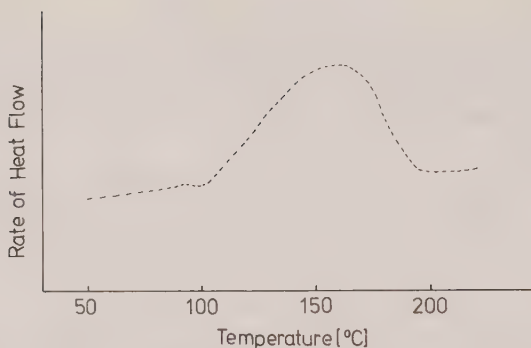


FIG. 7.8 Type of curve obtained from a DSC scan of melamine-formaldehyde resin-impregnated paper.

type of trace obtained when a melamine-resin-impregnated overlay paper is investigated by DSC at a scan rate of about $10^{\circ}\text{C}/\text{min}$. The crosslinking reactions are initiated at about 100°C and are complete at about 200°C . The area under the exothermic peak is proportional to the heat of reaction.

Since the crosslinking reactions are of the condensation type and the emission of volatile products would produce an endothermic peak in the DSC trace, these resins are normally studied using sealed cells.^{11,12}

Kinetic parameters can be derived from a DSC scan by several methods.^{13,14} The method of Rogers and Smith¹⁴ is usually satisfactory. The kinetics of the reaction or, more correctly, the reactions, are assumed to be of the following form:

$$\frac{dF}{dt} = A \exp \left[-\frac{E}{RT} \right] (1 - F)^n$$

where F is the fractional extent of conversion, A is the pre-exponential factor of the Arrhenius equation, E is the energy of activation, R the universal gas constant, T is absolute temperature and n is the apparent order of reaction.

It is assumed that the fraction of reaction which has occurred up to a particular temperature or time in a DSC scan is given by:

$$F = \frac{H}{H_t}$$

where H is the heat evolved up to that point and H_t is the total heat evolved during cure.

This definition of the fraction of reaction can be substituted into the general kinetic equation to give the following:

$$\frac{dH/H_t}{dt} = A \exp \left[-\frac{E}{RT} \right] (1 - H/H_t)^n$$

This equation can be differentiated and rearranged to give:

$$\frac{(-H/H_t) d/dt(dH/dt)}{\beta(dH/dt)^2} = \frac{E(1 - H/H_t)}{dH/dt \cdot RT^2} - \frac{n}{H_t}$$

where β is the scan speed.

This equation can be plotted in linear form to give a line of slope E/R and intercept n/H_t . It is normal to collect the data representing temperature and rate of heat flow (dH/dt) on punched tape¹¹ or directly on to a laboratory computer. Values of E , n and A can then be computed from the above equations.

These basic kinetic parameters can be used to predict the relationship between cure and time at constant or varying temperature. Figure 7.9 shows some curves of percentage cure against time at 130°C for a melamine resin containing three different concentrations of a particular catalyst, trimethylamine sulphur trioxide.

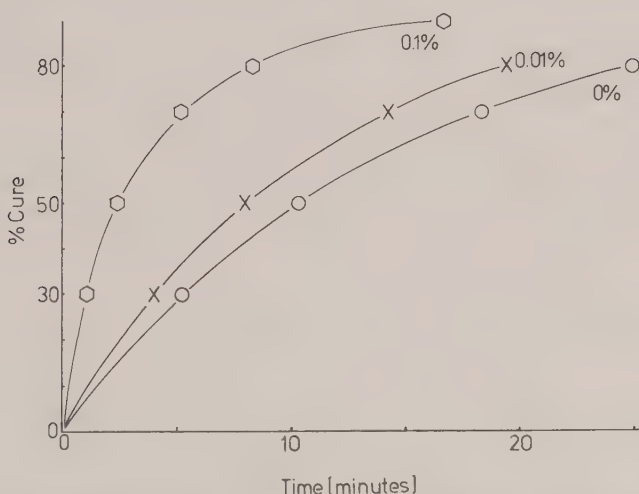


FIG. 7.9 Curves of degree of reaction against time at 130°C for BL 34 Resin (B.I.P. Ltd.) containing different concentrations of trimethylamine sulphur trioxide catalyst.

Kinetic data from DSC can be used to calculate the degree of cure in a press cycle such as that shown in Fig. 7.2. Press cycles can be optimised for particular resin-impregnated papers.

Fundamental studies of the flow properties of melamine and phenolic resins during cure are not so commonly measured as the cure itself. However, chemo-rheological investigations of epoxide resins used in glass reinforced laminates are often made^{15,16} and similar studies have been carried out upon resins used in powder coatings.¹³ Apart from the problems associated with the emission of volatile products during cure, similar investigations can be made upon melamine and phenolic resins. During lamination, the viscosity of the resins varies with both temperature and time and, in principle, the methods of White¹⁵ and Roller¹⁶ can be used to predict changes during a press cycle from a series of isothermal viscosity/time measurements made at different temperatures.

The importance of flow can be illustrated in the case of melamine-formaldehyde resins used in the overlay ply of a decorative laminate. Figure 7.10 shows the viscosity/time curves obtained for a melamine resin at 120°C and at four different levels of trimethylamine sulphur trioxide catalyst. The curves were obtained at low shear rate on a Ferranti-Shirley cone and plate viscometer. Clearly, the sharp increase in

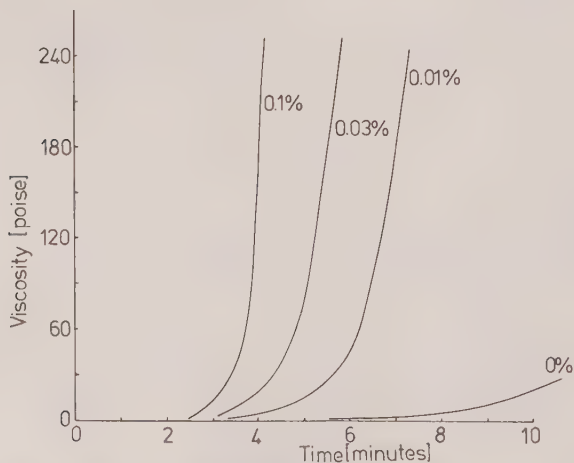


FIG. 7.10 Curves of viscosity against time at 120°C for BL 34 Resin (B.I.P. Ltd.) containing different concentrations of trimethylamine sulphur trioxide catalyst.

viscosity which accompanies the approach of gelation occurs after shorter time intervals as a greater concentration of this catalyst is included. The effect of the change in flow characteristics can be seen in terms of the wear properties of laminates made from overlays containing different levels of catalyst. Table 7.2 shows the wear resistance of such a series of laminates measured as the number of revolutions required to remove the surface ply using a Taber Abraser. Also shown in the table are the thicknesses of the surface plies as measured under a microscope.

As the flow of the surface resin is reduced, less sinkage occurs during lamination and a greater concentration of resin is retained in the surface layer. It is worth mentioning that at the highest concentration of catalyst, 1% w/w of resin, the flow of the resin is reduced to such an extent that a surface with poorer gloss milky areas results.

TABLE 7.2

EFFECT OF CATALYST CONCENTRATION UPON THE FLOW OF THE MELAMINE-FORMALDEHYDE RESIN IN THE OVERLAY PAPER

<i>% Trimethylamine sulphur trioxide (w/w of resin)</i>	<i>Wear resistance (revolutions)</i>	<i>Thickness of surface ply (μm)</i>
0	331	58
0.01	341	67
0.1	436	78
0.5	540	83
1.0	540	85

The measurement of flow and cure properties of resins used to prepare decorative laminates is central to the development of new resins, the optimisation of press cycles and the attainment of satisfactory decorative and physical properties in the laminate.

7.5 DEVELOPMENTS IN PAPER-BASED LAMINATES

7.5.1 Printed Circuit Board Laminates

There are limits to the electrical properties which can be attained from paper-based laminates. This is due to the tendency of cellulose to absorb moisture. If better electrical properties are required, laminates prepared from glass reinforced epoxide, polyester or polyimide resins would most

commonly be used. Improvements in paper-reinforced laminates for the manufacture of printed circuit boards have been mainly concerned with achieving better processibility or greater resistance to fire.

The holes which are made in paper-phenolic printed circuit board laminates for insertion of electronic component wires are normally produced by punching (see Chapter 6). Phenolic resins are inherently brittle and, in the past, it was normal to heat the laminate before punching in order to avoid cracking around the edges of holes. This is obviously inconvenient and time consuming. Laminates which can be punched at room temperature were desirable and have therefore been developed.

The most common method of flexibilising phenolic resins to achieve cold punching properties has been the incorporation of tung oil, also known as china wood oil, into the resin. Tung oil is a mixture of triglycerides in which about 70–80% of the fatty acid chains are derived from α -elaeostearic acid. This acid contains three conjugated double bonds. When tung oil is reacted with phenol or phenolic resoles, it becomes attached to the aromatic ring by a Friedel–Crafts alkylation process. The presence of the long aliphatic chains within the structure of the cured phenolic resin increases toughness and flexibility. Other unsaturated oils have been used and, more recently, synthetic polymers such as polybutadiene, polyisoprene or polyethylene glycols^{17,18} have been incorporated into phenolic resins in order to improve punching properties.

There are standard test methods for assessing the punching quality of laminates.¹⁹ These consist of observing defects such as cracking or ‘haloing’ after punching standard patterns of circular, square and diamond-shaped holes. Other workers have attempted to measure the forces associated with the punching of laminates. Learmonth and Watson^{20–22} used an instrumental punch and die rig and were able to obtain stress/strain curves associated with the punching process. They investigated the interactions between resins and reinforcements and the effect of temperature upon the stress/strain relationship. Learmonth and Watson also established an assessment of hole quality in which points are allocated on a scale of 0 to 6 by reference to a set of standard photographs.

In addition to the use of unsaturated oils or synthetic polymers, which can be reacted with phenolic resins, external plasticisers are also used to improve punching properties. These are often aromatic esters of phosphoric acid, such as tricresyl, triphenyl or diphenylcresyl phosphates.

These plasticisers also reduce the flammability of paper-based phenolic resin laminates.

The increased emphasis upon low flammability has been associated particularly with the introduction of colour television sets. These operate at higher temperatures and higher voltages than monochrome sets. There is therefore an increased risk of fire. The need for improved fire retardance has caused the introduction of additional specifications and test methods such as that of the Underwriter's Laboratory UL-94 vertical burning test. On the basis of this test fire retardant laminates are specified in order of decreasing flammability as V-1 or V-0.

The additives employed to improve fire retardancy normally contain phosphorus, nitrogen, halogens or antimony.²³ In fact, it is usual for a combination of these elements to be present.

Pre-impregnation of the paper reinforcement by melamine resins or the use of paper loaded with inorganic fillers, antimony trioxide or polyvinyl chloride have been commonly employed as methods of reducing flammability. As mentioned earlier, aromatic phosphates help to improve punchability and low flammability. Brominated compounds such as octabromodiphenyl, pentabromophenol and pentabromodiphenyl ether are also often used. Combinations of antimony trioxide with halogen-containing compounds are used since antimony and halogens exhibit a synergistic effect. This is due to the formation of antimony halides and oxyhalides during combustion. The formation of these halides causes a delay in the escape of halogens from the flame.

Chlorine- or bromine-containing compounds produce hydrogen chloride and hydrogen bromide, respectively, during combustion. These gases are both toxic and corrosive. For these reasons, the current trend is to reduce the level of halogens in fire retardant laminates.

7.5.2 Decorative Laminates

Much of the improvement in decorative laminates during recent years has been in their aesthetic appeal. There have been considerable improvements in the printing of the decorative sheet. This is usually produced using the technique of rotogravure. There have been improvements in the cylinder production and the registration control upon printing machines. These have caused the improvements in the clarity and reproduction of patterns.

There has also been more emphasis upon textured laminates with, for example, slate, leather, basketwork or cork simulations. Efforts are being made to accurately coordinate texture with design.

Important though these developments have been since decorative laminates are largely sold on the basis of their appearance, they do not represent changes in the physical properties of laminates. They are therefore outside the scope of a book concerned with developments in reinforced plastics. Two areas of development requiring changes in raw materials and producing laminates with different physical properties are represented by post-forming laminates and laminates with improved scratch or wear resistance. These will be discussed in greater detail.

Post-forming laminates. Post-forming laminates are manufactured as flat sheets in the same manner as conventional high pressure laminates. However, they can be formed into simple curves after lamination. Although such laminates have been available for more than two decades, it was only during the 1970s that they began to be used in kitchen furniture, at least in Europe. Post-forming laminates have been used extensively for several years longer in the USA.

Laminates are post-formed after heating to a temperature usually between 140 and 175°C. The laminate is normally bonded to a preshaped substrate so that some laminate extends beyond the edge of the substrate. It is then heated, usually by infra-red lamps, to the required temperature and formed over the substrate by pressure from a forming bar in a continuous process. As the laminate exits from the forming zone it is held with rollers against the substrate surface and pressure is maintained until the adhesive cools or cures.

Post-forming laminates differ from standard laminates in terms of the raw materials employed and sometimes the press cycle. In addition, post-forming laminates are often thinner (perhaps less than 1 mm) than standard laminates which are commonly 1.3–1.5 mm thick. This helps the forming of bends of low radius.

The type of paper used to prepare post-forming laminates is often similar to that used in standard laminates. However, in the USA, it has been common practice to include plies of highly extensible X-crepe paper. This is creped in two directions each of which is about 45° to the machine direction of the paper.

The resins within a post-forming laminate have to be softer than those of a standard laminate. There are several ways in which this may be achieved. Phenolic resins are often formulated at low molar ratios of formaldehyde to phenol, perhaps 1:1 or 1.2:1, and catalysts such as ammonia or primary and secondary amines can be used. These catalysts modify the final structure of the resin and improve formability.²⁴ In the

case of melamine resins there is a limit to the reduction of the ratio of formaldehyde to melamine due to the solubility characteristics of the latter. Plasticisers, such as *p*-toluene sulphonamide, polyethylene glycols or polyvinyl acetate, can be used. Another approach involves the replacement of some of the melamine with a triazine of lower functionality. An example is acetoguanamine in which one of the amine groups present in melamine is replaced by a methyl group.²⁵

A reduction in the crosslink density of the phenolic and melamine resins can also be achieved by control of the press cycle or resin reactivity. Shorter cycle times or lower peak temperatures can be used to limit the extent of cure and melamine resins can be buffered at relatively high pH to reduce reactivity and thereby provide easier control of the final state of cure.²⁶

If resins are well formulated, it is possible to achieve good post-formability with very little reduction in the desirable properties of water resistance, scratch and wear characteristics or heat resistance which are normally associated with high pressure decorative laminates.

Scratch and wear resistance. High pressure decorative laminates exhibit good scratch and wear resistance properties, and this has been one of the main reasons for their acceptance in kitchen furniture and for such uses as bank counters or supermarket check-outs in which coins or metal baskets are drawn across their surfaces. Melamine-formaldehyde resins are relatively hard compared with many synthetic plastics. Table 7.3 shows a comparison of the Rockwell hardness (α -scale) of several thermoset and thermoplastic polymers.^{27,28}

The hardness of a material is by no means the only factor which

TABLE 7.3
COMPARISON OF HARDNESS VALUES FOR SOME THERMOPLASTIC AND
THERMOSET POLYMERS

<i>Polymer</i>	<i>Rockwell hardness (α-scale)</i>
Poly(methylmethacrylate)	102
Polystyrene	109
MF resin	130
MF resin/cellulose laminate	115
PF resin (wood flour filled)	120
Nylon 6,6	102
Cellulose acetate	68

determines scratch resistance. Ratner²⁹ has shown that the tensile breaking stress and elongation at failure are important. However, it is probable that the good scratch resistance of decorative laminates is primarily due to the hardness of the melamine surface.

Many attempts have been made to improve the scratch and wear properties of high pressure laminates in order that they should better withstand the harshest conditions under which they are already used, and perhaps extend their areas of application.

The usual approach has been to include within the melamine surface a hard mineral such as alumina or silica. This has been achieved by passing overlay paper through a colloidal dispersion of silica particles in a melamine-formaldehyde resin³⁰ or by making a two layer paper, the surface layer of which contains a mineral of Mohs scale hardness of at least 7.³¹

The preparation of a satisfactory dispersion of mineral particles in resin is not easy, and the use of a mineral filled paper depends upon the paper suppliers. For these reasons, laminate producers have attempted to prepare laminates with mineral filled surfaces by another method. Several patents describe a technique of coating the print paper with a mixture of resin, cellulose fibre and mineral.³²⁻³⁶ The coating mixture usually contains a thickening or thixotropic additive to prevent too much absorption or penetration into the print paper. It is necessary to include cellulose in the formulation to avoid the problem of crazing which occurs with melamine resin alone under changing humidity conditions. The mineral filler has to be hard and of about the same refractive index as melamine resin in order that the protective coating is transparent.

There is little doubt that the presence of a hard mineral filler improves scratch and wear resistance. This can be demonstrated by comparing the wear of such materials and conventional laminate, side by side, in a real situation in which the laminates are severely abused. However, many of the claims in the literature are exaggerated. This is due to the test method normally employed to measure wear resistance.

The usual tests (e.g. ref. 37) are based upon a Taber Abraser. The laminate is placed upon the turntable of the apparatus and specified abrasive paper is attached to the wheels under which the sample is rotated. It has been shown by Rhee and Dumbleton^{38,39} that the minerals in a laminate surface damage the abrasive particles (alumina) in the paper and therefore cause it to be ineffective. If the abrasive paper is

changed frequently during the test, the difference between laminates with filled and unfilled surfaces is much reduced. The standard methods commonly require the abrasive tape to be changed after 500 revolutions. Rhee and Dumbleton showed that for mineral filled laminate surfaces a change after each series of 50 revolutions is much more realistic.

7.6 CONCLUSIONS

Paper-based laminates for decorative, electrical and constructional applications have been manufactured for many years. During this time raw materials and the manufacturing process have been optimised in terms of cost and performance. There is no compelling reason for changing the basic components and satisfactory properties such as the post-formability of decorative laminates or the punching characteristics of printed circuit board laminates have been achieved by modification of resins rather than by substitution with an alternative.

Improvements will continue to be made in the aesthetic qualities of decorative laminates. These will be achieved by better photographic and printing techniques rather than radical changes in raw materials. The trend towards laminates with more deeply textured surfaces will require more basic understanding of the flow properties of resins and perhaps an improvement in the flexibility of surface papers.

Paper-phenolic laminates for printed circuit board production will continue to be used as a cheap and satisfactory alternative to epoxide-glass laminates. It is probable that different fire retardant additives will be required in the future because of the corrosive and toxic properties of the combustion products of brominated compounds. There will probably be a trend towards the use of additive circuitry rather than the conventional subtractive circuitry. In other words, the copper tracks will be plated on to the surface of the laminate where required instead of the great majority of the copper on a copper-clad laminate being etched away. This will obviously lead to a decrease in the production of copper-clad laminates and the introduction of more paper-phenolic laminates with surfaces which can be activated to achieve deposition of copper from plating solutions. There are sound economic and environmental reasons for such a change in printed circuit board production methods.

At present, paper-based laminates containing phenolic and/or melamine resins provide most of the properties required of decorative

laminates or printed circuit board laminates for domestic electronic equipment. It is difficult to formulate products with similar technical properties without incurring a significant increase in cost.

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